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(54) Title: OXIDATIVE TREATMENT OF HAIR WITH REDUCED HAIR DAMAGE

(57) Abstract: The present invention relates to hair care compositions comprising chelants and methods for reducing oxidative hair damage. The compositions contribute to reducing the oxidative damage sustained by keratinous fibers such as human hair during bleaching, dyeing, perming or other oxidative treatments. The compositions according to the present invention also provide excellent color evenness and color fastness.

OXIDATIVE TREATMENT OF HAIR WITH REDUCED HAIR DAMAGE

5

FIELD

The present invention relates to hair care compositions comprising chelants and methods for reducing oxidative hair damage during oxidative treatments of hair such as bleaching, oxidative dyeing or perming.

BACKGROUND

Melanin is a natural pigment found in hair. Melanin and hair-forming cells are naturally produced in the hair bulb at the root of the hair. As new cells are produced, the older ones are pushed upwards out of the skin to form the hair shaft, which is the part of the hair that can be seen above the scalp. Hair can be schematically described as being made of a center part called the cortex, which contains the melanin, and an outer layer called the cuticle. It is the cortex that gives hair its special qualities such as elasticity and curl.

The hair shaft is made of dead cells that have turned into a mixture of different forms of the special hair protein, keratin. Keratin contains high concentrations of a particular amino acid called cystine. Every cystine unit contains two cysteine amino acids in different chains, which have come to lie near each other and are linked together by two sulphur atoms, forming a very strong chemical bond known as a disulphide linkage. This cross-linking by disulphide linkages between the keratin chains accounts for much of the strength of the hair.

Bleaching and dyeing (or coloring) of hair has become increasingly popular over the past years. Younger people may want to change the natural color of their hair to a more fashionable one, while older people may also use dyeing compositions to conceal gray hair. As people grow older, the production

of melanin slows, giving more and more gray hair over time. Melanin can be purposely altered by chemical treatments to give lighter shades. The lightening is achieved by oxidizing the melanin pigments, usually with an oxidizing agent in alkaline solution, also called bleaches. Examples of oxidizing agents that can be
5 used are hydrogen peroxide, potassium, sodium or ammonium salts of perborate or percarbonate, persulfate and percarbamide.

Bleaches are also used during oxidative dyeing treatments. Oxidative (or "permanent") dye compositions comprise "precursor dyes" which are small molecules capable of diffusing into the hair. These molecules mainly belong to
10 three classes of aromatic compounds: diamines, aminophenols and phenols. They are sufficiently small to diffuse in the hair shaft where, once activated by an oxidizing agent such as hydrogen peroxide, they further react with other precursors to form larger colored complexes. Oxidative hair dye compositions commonly contain, in addition to the dye precursors and a source of peroxide, a
15 variety of additional cosmetic and peroxide stabilizing agents.

Oxidizing agents can activate oxidative dye precursors across a range of pH. However, it is known that enhanced dye oxidation can be achieved via the use of a hair-swelling agent (HSA) that can adjust the pH of the oxidizing solution. Such HSA's further enhance the oxidizing and dyeing process by
20 swelling the hair fibers to aid both the diffusion of the peroxide and dyeing agents into the hair and enabling faster, more thorough dye oxidization and hair dyeing. Preferred hair-swelling agents for adjusting the pH of peroxide hair oxidizing compositions are aqueous alkaline solutions containing ammonia (ammonium hydroxide) or monoethanolamine(MEA).

25 Low levels of chelants are routinely used as stabilizers or preservatives in various oxidizing compositions. For example, EDTA (ethylenediaminetetraacetic acid) is commonly used as a stabilizer in hydrogen peroxide solution, which would otherwise decompose too rapidly and could not be stored for a long time. Ethylene diaminedissuccinic acid (EDDS) is also known as a good stabilizing
30 agent component to increase the stability of laundry bleaching products.

Amounts as low as 0.1% by weight of the oxidizing composition are usually used to stabilize the oxidizing agent contained in said oxidizing compositions.

Oxidative treatments of hair such as bleaching (decoloration) and oxidative dyeing give good results and are very commonly used. They are 5 however not without drawbacks. The oxidizing agents used for bleaching and oxidative dyeing damage hair to some extent. The mechanism by which damage is caused to the hair fibers is not perfectly understood. However, it is known that some of the disulphide bonds linking the keratin chains break in the presence of oxidizing compositions. Repeated oxidative treatments leave weak, brittle hairs, 10 which have little shine and luster. An enormous effort has been made to address this problem over the past years, and various solutions have been proposed.

Today, most dyeing or bleaching compositions are sold with a conditioner, which is applied on hair after the bleaching or dyeing composition has been rinsed off. Examples of conditioning agents are silicones, cationic surfactants 15 and cationic polymers. However efficient, conditioners cannot prevent successive chemical treatments causing premature hair breakage. In fact, conditioners do not bring the hair back to its initial condition but merely conceal the damage under a protective layer of the conditioning agent, which only results in an improved feel of the hair.

20 Attempts have been made to protect the hair from damage instead of merely concealing it. US 5,100,436 discloses hair dyeing compositions comprising metal-chelant complexes. The use of catalytic amounts of dipyridyl or o-phenanthroline complexes (0.001 to 0.1% by weight of the solution) allows a reduction in the time of exposure, thus reducing the damage caused by the 25 oxidizing agent.

US 6,013,250 discloses composition for treating hair against chemical and photo damage by the use of hydrolyzed proteins having an abundance of anionic amino acids and in particular, sulphur-containing amino acids. These proteins serve as "decoys", in order to minimize the damage caused to the natural 30 disulphide bonds.

US4,138,478 discloses agents for reducing the damage to hair during bleaching and dyeing by the use of a water-soluble 3-amino-1-hydroxypropane-1,1-diphosphonic compound for protecting hair from damage by "nascent oxygen". According to this patent, "the diphosphonic compound is substantively adsorbed by the hair and acts to hinder degradation of the hair by nascent oxygen which is either present therewith or which is substantially added". Other protective compounds such as hydroxyethane-1,1 diphosphonic acid (HEDP) and ethylenediaminetetramethylene phosphonic acid (EDTMP) are disclosed at low levels in US3,202,579 and US3,542,918.

10 "Properties of peroxide-bleached hair" (W.Edman & E.Marti, J. Soc. Cosmet. Chem., 1960, p.133), discloses that an aqueous solution of hydrogen peroxide is stabilized by adding 0.1% by weight of the bleaching composition of tetrasodium salt of EDTA (ethylenediamine tetraacetic acid) and that damage to hair can be prevented by adding 0.1% of the tetrasodium salt of EDTA to the
15 aqueous bleaching compositions. However, it has now been surprisingly found that EDTA, although widely used in bleaching and dyeing compositions, displays very little benefits, unless utilized at levels much higher than 0.1%.

Chelants in hair care compositions have been used to remove minerals bound to hair. For example, US 5,635,167 discloses a process for the removal of
20 exogenous metal ions that have become attached to hair. The treatment comprises a step wherein hair is contacted with a blend of chelating agents (selected from the group consisting of amino acid chelating agents, polyphosphate chelating agents and phosphonate chelating agents) at a pH of between 4 and 9 and at a concentration of between 4% to 25% by weight.

25 WO97/24106, Dias et al. discloses hair coloring compositions comprising a water soluble peroxygen-bleach, a bleaching aid selected from organic peroxyacid bleach precursors and preformed organic peroxyacids and one or more hair coloring agents. Various chelants are disclosed as optional ingredients and exemplified in hair care compositions at 0.1% by weight of the composition.
30 The organic peroxy acid bleach precursors are defined as organic compounds that react with hydrogen peroxide in a perhydrolysis reaction to produce a

peroxyacid. These bleaching aids are claimed to provide benefits including reduced hair damage at lower pH. However, the Applicant has found that at a pH higher than 8, these bleaching aids are much more damaging to hair than usual water-soluble oxidizing agents such as hydrogen peroxide. Without being bound by theory, the Applicant believes that the conjugate base of the organic peroxyacid formed at a pH above 8 is more likely to oxidize the disulphur bonds of the keratin than other oxidizing agents such as hydrogen peroxide. Additionally, hair coloration, especially with oxidative dyes is much poorer at pH 8 than pH 10, which is another advantage of this invention over WO9724106.

10 Finally peroxyacid precursors are difficult to solubilize, especially in oil-in-water emulsion.

Despite these developments, damage to hair caused by the strongly aggressive chemicals contained in most bleaching, dyeing or perming compositions particularly with repeated usage is still a problem, particularly at 15 high pH.

It is hence an object of the present invention to provide new compositions capable of improved protection of keratinous fibers such as human hair from oxidative damage, in particular the structurally important keratin bonds such as the disulphide bonds from oxidative breakage.

20 It is another object of this invention to provide bleaching, dyeing or perming compositions with a better efficiency in terms of light shade, color evenness, color fading and hair feel.

It is another object of this invention to provide bleaching or dyeing compositions capable of protecting keratinous fibers such as hair while at the 25 same time delivering a good lightening effect.

It is another object of the present invention to provide methods of treating hair with chelants for reducing oxidative hair damage.

It has now been surprisingly found that chelants have excellent damage inhibiting properties. None of the above-mentioned references disclose the 30 compositions of the present invention.

SUMMARY

The subject of the present invention is a composition suitable for use during a hair treatment comprising:

- a) an oxidizing agent;
- 5 b) a chelant;

wherein said chelant is in an amount sufficient to provide a damage benefit equivalent to less than 160, preferably less than 140, more preferably less than 120, even more preferably less than 110 cysteic acid units as measured by the FT-IR Damage Assessing Protocol after a 5-Cycle Oxidative Hair Treatment

10 Protocol With 2 Intermediate Washes as defined herein and/or to provide a damage benefit equivalent to a Normalized Shine Ratio of at least 0.80, preferably at least 0.85, more preferably at least 0.95, even more preferably at least 0.99 as measured by the Goniophotometer Damage Assessing Protocol after a 5-Cycle Hair Oxidative Treatment Protocol With 10 Intermediate Washes

15 as described herein.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

20 As used herein the term "hair" to be treated may be "living" i.e. on a living body or may be "non-living" i.e. in a wig, hairpiece or other aggregation of non-living keratinous fibers. Mammalian, preferably human hair is preferred. However wool, fur and other keratin containing fibers are suitable substrates for the compositions according to the present invention.

25 As used herein, the term "oxidizing composition" means a composition comprising at least one oxidizing agent suitable for use on hair, such as hydrogen peroxide, sodium, potassium, ammonium or other salts of perborate, percarbonate, persulfate and percarbamide. Examples of such compositions are oxidative dye compositions and bleaching compositions.

As used herein the term "oxidative treatment of hair" or a "hair treatment comprising at least one oxidative step" is used in the broad sense in that it is intended to encompass all treatments of hair comprising at least one step of contacting hair with at least one oxidizing composition. Examples of oxidative treatment for human hair are bleaching, dyeing or perming.

5 As used herein the term "immediately" means within about 1 hour, preferably within about 30mn, more preferably within about 15mn.

As used herein the term "log x" refers to the common (or decimal) logarithm of x.

10 All percentages are by weight of the total composition unless specifically stated otherwise. When more than one composition are used during a treatment, the total weight to be considered is the total weight of all the compositions applied on hair simultaneously (i.e. the weight found "on head") unless otherwise specified. All ratios are weight ratios unless specifically stated otherwise.

15 All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Chelants

Definition

20 The term "chelant" (or "chelating agent" or "sequestering agent") is well known in the art and refers to a molecule or a mixture of different molecules each capable of forming a chelate with a metal ion. A chelate is an inorganic complex in which a compound (chelant) is coordinated to a metal ion at two or more points so that there is a ring of atoms including the metals. Chelants 25 contain two or more electron donor atoms that form the coordination bonds with the metal ion.

Chelants are well known in the art and a non-exhaustive list thereof can be found in AE Martell & RM Smith, Critical Stability Constants, Vol. 1, Plenum Press, New York & London (1974) and AE Martell & RD Hancock, Metal

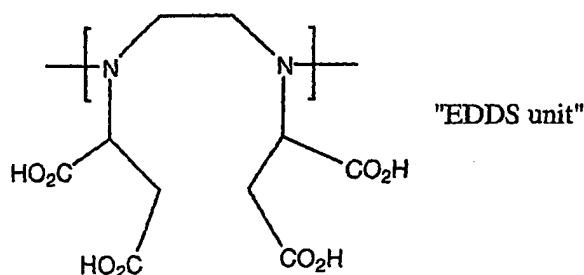
Complexes in Aqueous Solution, Plenum Press, New York & London (1996) both incorporated herein by reference.

When related to chelants, the terms "salts and derivatives thereof" mean all salts and derivatives comprising the same functional structure as the chelant

5 they are referring to and that have similar or better chelating properties. These terms include alkali metal, alkaline earth, ammonium, substituted ammonium salts (e.g monoethanolammonium, diethanolammonium, triethanolammonium), esters of chelants having an acidic moiety and mixtures thereof, in particular all sodium, potassium or ammonium salts. The term "Derivatives" also includes

10 "chelating surfactant" compounds (these are chelants modified to bear a surfactant moiety while keeping the same chelating functionality, see US5284972, "N-acyl-N,N',N'-ethylenediaminetriacetic acid" for an example of modified ethylenediaminetriacetic acid). The term "Derivatives" also includes large molecules comprising one or more chelating groups having the same

15 functional structure as the parent chelants. Examples of these large molecules is polymeric EDDS (ethylenediaminedisuccinic acid) made of unit block according to the following structure:



and disclosed in US5,747,440 Kellett et al.

20 Preferred chelants for use herein are carboxylic acids (in particular aminocarboxylic acids), phosphonic acids (in particular aminophosphonic acids) and polyphosphoric acids (in particular linear polyphosphoric acids), their salts and derivatives.

Aminocarboxylic acid chelants

Carboxylic acid chelants as defined herein are chelants having at least one carboxylic acid moiety (-COOH).

Examples of aminocarboxylic acid chelants suitable for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as diethylenetriamine 5 pentaacetic acid (DTPA), ethylenediamine disuccinic acid (EDDS), ethylenediamine diglutaric acid (EDGA), 2-hydroxypropylenediamine disuccinic acid (HPDS), glycamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglyutaric acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), ethylenediaminetetraacetic acid (EDTA), salts thereof and derivatives 10 thereof.

Other suitable aminocarboxylic chelants for use herein are iminodiacetic acid derivatives such as N-2-hydroxyethyl N,N diacetic acid or glyceryl imino diacetic acid (described in EP-A-317,542 and EP-A-399,133), iminodiacetic acid- 15 N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid (described in EP-A-516,102), β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid chelants (described in EP-A-509,382), ethanoldiglycine acid, salts thereof and derivatives thereof.

EP-A-476,257 describes suitable amino based chelants. EP-A-510,331 20 describes suitable chelants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid chelants. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable.

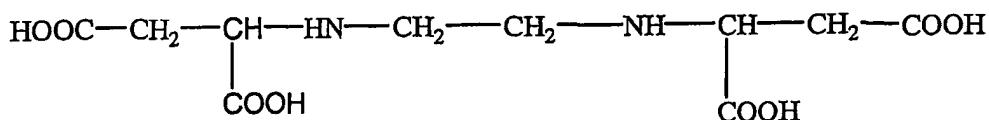
Preferred aminocarboxylic chelants are diamine-N,N'-dipolyacid and monoamine monoamide-N,N'-dipolyacid chelants, salts thereof and derivatives 25 thereof. Preferred polyacids contain at least two acid groups independently selected from the carboxylic acid group (-COOH), sulphonic group (-SO₃H), the o-hydroxyphenyl group, the m-hydroxyphenyl group and the p-hydroxyphenyl group. Suitable polyacids include diacids, triacids and tetraacids, preferably diacids. Preferred salts include alkali metal, alkaline earth, ammonium or 30 substituted ammonium salts. EDTA is a tetramonoacid and does not belong to this class of preferred chelants.

Preferably, the polyacids are di-carboxylic acids, preferably di-carboxylic acids having a carbon chain length of from about 3 to about 10 carbon atoms, more preferably from about 4 to about 6 carbon atoms, even more preferably about 4 carbon atoms.

Exemplary diamine dipolyacids suitable for use herein include ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-diglutaric acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDS), all disclosed in European Patent EP0687292, ethylenedicysteic acid (EDC) disclosed in US5,693,854, diaminoalkyldi(sulfosuccinic acids) (DDS) disclosed in US5,472,642 and EDDHA (ethylenediamine-N,N'-bis(ortho-hydroxyphenyl acetic acid)), a method of preparation of which is disclosed in EP331556. A preferred monoamine monoamide-N,N'-dipolyacid is glycinamide-N,N'-disuccinic acid (GADS), described in US 4,983,315.

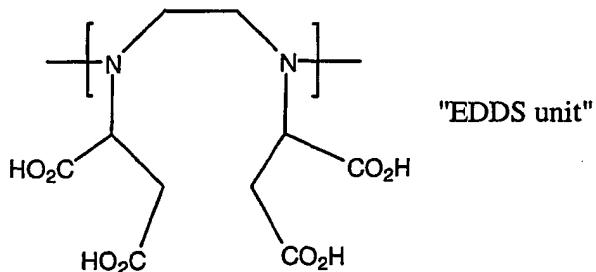
Highly preferred for use herein is ethylenediamine-N,N'-disuccinic acid (EDDS), derivatives and salts thereof. Preferred EDDS compounds for use herein are the free acid form, and salts thereof. Preferred salts include alkali metal, alkaline earth metals, ammonium and substituted ammonium salts (e.g. monoethanolammonium, diethanolammonium, triethanolammonium). Highly preferred salts are sodium, potassium, magnesium and calcium salts. Examples of such preferred sodium salts of EDDS include Na₂EDDS and Na₃EDDS.

The structure of the acid form of EDDS is as follows:

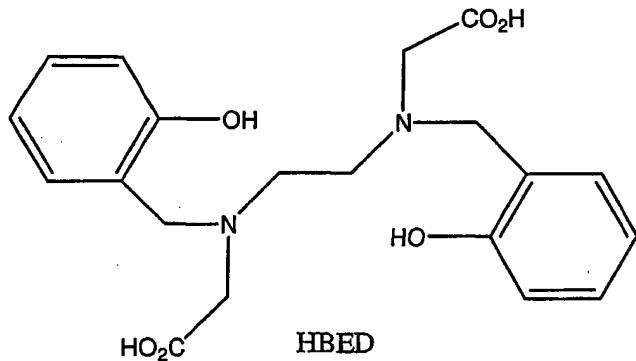


EDDS can be synthesised, for example, from readily available, inexpensive starting materials such as maleic anhydride and ethylenediamine. The synthesis of EDDS from maleic anhydride and ethylene diamine yields a mixture of three optical isomers, [R,R], [S,S], and [S,R] (25% S,S, 50% R,S and 25% R,R), due to the two asymmetric carbon atoms. The biodegradation of EDDS is optical isomer-specific, with the [S,S] isomer degrading most rapidly and extensively.

US5,747,440, Kellett et al., discloses EDDS derivatives comprising an modified polyamine having units of the formula:



Preferred aminocarboxylic acid chelants that are not diamine-N,N'-dipolyacid and monoamine monoamide-N,N'-dipolyacid chelants include N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED) salts thereof and derivatives thereof:



Examples of suitable HBED derivatives can be found in WO9744313.

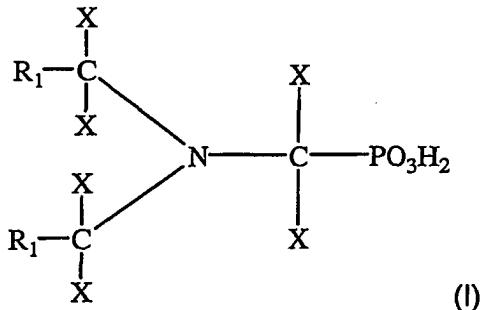
10 Polyphosphoric acid chelants

Suitable polyphosphoric acid type chelants include molecules that contain more than one P atom and have P-O-P bonds. Polyphosphoric acid chelants and salts (polyphosphates) can be linear and are generally represented by the formula $[P_nO_{3n+1}]^{(n+2)-}M_{(n+2)}^+$ wherein M is a suitable counter-ion such as H^+ , Na^+ or K^+ and n an integer. Polyphosphoric acid type chelants and their polyphosphate salts can also be cyclic and have the formula $[P_nO_{3n}]^n-M_n^+$. Representative examples include, among other, sodium tripolyphosphate, tetrasodium diphosphates, hexametaphosphoric acid and sodium metaphosphate.

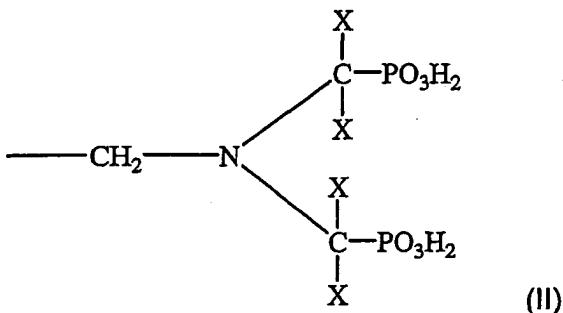
Phosphonic acid chelants

Suitable phosphonic acid type chelants include amino alkylene poly (alkylene phosphonic acid), ethane 1-hydroxy diphosphonic acids and nitrilo trimethylene phosphonic acids, salts thereof and derivatives thereof. Suitable 5 chelants of this type are disclosed in US 4,138,478, Reese et al., US 3,202,579 and US3,542,918, Berth et al, all incorporated herein by reference.

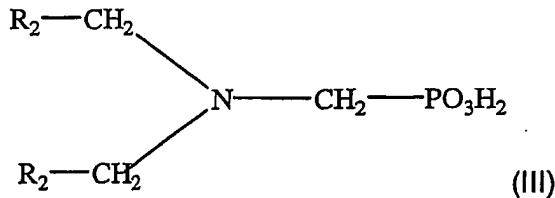
Preferred phosphonic acid type chelants for use herein have the formula (I) below:



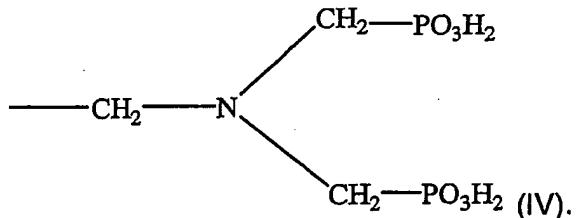
10 wherein each X are independently selected from hydrogen or alkyl radicals, preferably hydrogen or alkyl radicals having from 1 to 4 carbon atoms, preferably hydrogen; and each R₁ are independently selected from -PO₃H₂ or a group having the formula (II) below:



15 Preferred chelants according to Formula (I) for use herein are aminotri-(1-ethylphosphonic acid), ethylenediaminetetra-(1-ethylphosphonic acid), aminotri-(1-propylphosphonic acid), aminotri-(isopropylphosphonic acid) and chelants having the formula (III) below:



wherein each R_2 are independently selected from $-\text{PO}_3\text{H}_2$ or a group having the formula (IV) below:



5 Especially preferred chelants according to formula (III) for use herein are aminotri-(methylenephosphonic acid), ethylene-diamine-tetra-(methylenephosphonic acid) (EDTMP) and diethylene-triamine-penta-(methylenephosphonic acid) (DTPMP).

Examples of other chelants:

10 Examples of other chelants suitable for use herein include but are not limited to polyethylenimines as disclosed in US5,955,415.

Levels

Chelants must be present in the composition at a level sufficient to provide a benefit measurable by the FT-IR Damage Assessing Protocol after a 5-Cycle Oxidative Hair Treatment Protocol With 2 Intermediate Washes and/or by the Goniophotometer Damage Assessing Protocol after a 5-Cycle Hair Oxidative Treatment Protocol With 10 Intermediate Washes, both of which are defined herein.

20 Levels of chelants in the oxidizing compositions or in pre-treat compositions can be as low as about 0.25%, preferably at least about 0.5% for the most effective chelants such as diamine-N,N'-dipolyacid and monoamine monoamide-N,N'-dipolyacid chelants (for example EDDS). Less effective chelants will be more preferably used at levels of at least about 1%, even more

preferably above about 2% by weight of the composition, depending of the efficiency of the chelant. Levels as high as about 10% can be used, but above this level significant formulation and/or human safety issues arise. Levels above about 4% can be used but will usually not result in additional damage benefit.

5

Damage prevention

The Applicant has surprisingly found that chelants could efficiently prevent oxidative hair damage when formulated in level higher than previously mentioned in the literature or formulated in commercial compositions. Levels of chelants used in the prior art are, at best, too low to be really useful and sometimes totally inefficient (See Experimentals). This is particularly true for formulations with rheologies greater than water such as oil-in-water emulsions or thickened aqueous solutions.

10. 15.

Oxidative hair damage can be measured by the FT-IR Damage Assessing Protocol and/or by the Goniophotometer Damage Assessing Protocol, both described below.

It is was found that it is highly relevant for the consumer that oxidizing compositions comprise a chelant or a mixture of chelants in an amount sufficient to provide a damage benefit equivalent to:

a) less than 160, preferably less than 140, more preferably less than 120,
20 even more preferably less than 110 cysteic acid units as measured by the FT-IR
Damage Assessing Protocol after a 5-Cycle Oxidative Hair Treatment Protocol
as defined below; and/or

b) a Normalized Shine Ratio of at least 0.80, preferably at least 0.85,
more preferably at least 0.95, even more preferably at least 0.99 as measured
25 by the Goniophotometer Damage Assessing Protocol after a 9-Cycle Hair
Oxidative Treatment Protocol as described herein.

Conditional Stability Constants of preferred chelants

Good results such as those described above can be achieved by increasing the levels of previously used chelants or by using level of select chelants that were found to be particularly efficient even at low levels. These
30

particularly efficient chelants have a much stronger affinity for transition metal ions such as Cu²⁺ than for alkaline-earth metal ions such as Ca²⁺ at pH 10. One relatively easy way of predicting how well a chelant will perform is calculating the ratio of the log of the Conditional Stability Constant of the chelant for Cu²⁺ to the 5 log of the Conditional Stability Constant of the chelant for Ca²⁺ at pH 10 as described below.

The Conditional Stability Constant is a parameter commonly used in the art to practically assess the stability of metal-chelant complex at a given pH. A detailed discussion on Conditional Stability Constant can be found for example in 10 "Dow chelating agents" published by the Dow Chemical Company Limited, incorporated herein by reference.

The Stability constant of a metal chelant interaction can be defined as:

$$K_{ML} = \frac{[ML]}{[M][L]}$$

15 Where:

[ML] = Concentration of metal chelant complex at equilibrium

[M] = Concentration of free metal ion

[L] = Concentration of free chelant

K_{ML} = Stability constant for the metal chelant complex

20 Wherein all concentrations are expressed in mol/dm³. Stability constants are conveniently expressed as logarithms. The values of the logarithms of the Stability constant values for some exemplary metal ion - chelant complexes are given in the following table:

Table 1 - Log Stability constants for 1:1 complexes of various chelants
25 with Cu and Ca [1] (fully deprotonated chelants)

<u>Agent</u>	<u>log K*</u>	
	<u>Cu</u>	<u>Ca</u>
EDDS	18.35	4.58
DTPMP	19.5	7.1

EDTMP	23.2	9.36
DTPA	21.4	10.75
HEDP	11.84	6.0
EDTA	18.78	10.65
EDDHA	25.3	7.2

* All measured at 25deg and 0.1M ionic strength

Most chelants have a degree of protonation that is dependent on pH. This can be expressed using chelant proton Stability constants (stepwise K).

These Stability constants are obtained from the equation below:



5

The values of the proton chelant Stability constant for some usual chelants are given in the tables below:

Table 2a - log protonation constants for tetra-protonated chelants [1]

	HL ³⁻	H ₂ L ²⁻	H ₃ L ⁻	H ₄ L
EDDS ⁴⁻	10.01	6.84	3.86	2.95
HEDP ⁴⁻	10.8	6.88	2.53	1.8
EDTA ⁴⁻	10.19	6.13	2.69	2.00
EDDHA ⁴⁻	12.1	9.5	8.5	6.3

10

Table 2b - log protonation constants for penta-protonated chelants [1]

	HL ⁴⁻	H ₂ L ³⁻	H ₃ L ²⁻	H ₄ L ⁻	H ₅ L
DTPA ⁵⁻	10.48	8.60	4.28	2.6	2.0

Table 2c - log protonation constants for hepta-protonated chelants [1]

	HL ⁶⁻	H ₂ L ⁵⁻	H ₃ L ⁴⁻	H ₄ L ³⁻	H ₅ L ²⁻	H ₆ L ⁻	H ₇ L
EDTMP ⁷⁻	13.0	9.78	7.94	6.42	5.17	3.02	1.30

15

Table 2d - log protonation constants for octa-protonated chelants [1]

	HL ⁷⁻	H ₂ L ⁶⁻	H ₃ L ⁵⁻	H ₄ L ⁴⁻	H ₅ L ³⁻	H ₆ L ²⁻	H ₇ L ⁻	H ₈ L

DTPMP ⁸⁻	12.0	10.10	8.15	7.17	6.38	5.50	4.45	2.8
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[1] = Arthur Martell & Robert M Smith, Critically Selected Stability Constants of Metal Complexes Database, Version 3.0

The stability constants of chelant-metal ion complexes are well documented in the literature for commonly used chelants (see for example = 5 Arthur Martell & Robert M Smith, Critically Selected Stability Constants of Metal Complexes Database, Version 3.0 and above, incorporated herein by reference). When not documented the constants can still be measured using various analytical methods (see "Metal Complexes in Aqueous Solutions", Martel and Hancock, edition Modern Inorganic Chemistry, p.226-228, incorporated herein by 10 reference).

The gradual change in chelant species as pH changes can be represented using alpha coefficients (α_{HL}), defined as

$$\text{Alpha coefficient (at a given pH)} = \frac{\text{Total concentration of ligand}}{\text{Free ligand concentration}}$$

In the case of tetra-acid chelants the values can be calculated from

$$15 \quad \alpha_{HL} = 1 + K_1[H] + K_1K_2[H]^2 + K_1K_2K_3[H]^3 + K_1K_2K_3K_4[H]^4$$

A further factor affecting metal chelant interactions is the tendency of metals to form hydroxide species as the pH increases. This effect can be represented using metal alpha values [2] as summarised in the table below at pH 10:

Table 3 - log alpha values for metal ions [2]

pH	Ca ²⁺	Cu ²⁺
10	0.0	2.00

20 [2] = A Ringbom & E Wanninen, Treatise on Analytical Chemistry, 2nd Ed, 1979, Part 1, Vol 2

By combining Stability constants and alpha constants at pH 10 we can use the formula below to give the effective chelating power of a chelant. This is the Conditional Stability Constant referred to in this Patent Application.

$$25 \quad K_{ML(\text{cond})} = \frac{K_{ML}}{\alpha_M \cdot \alpha_{HL}} \quad \log K_{ML(\text{cond})} = \log K_{ML} - \log \alpha_{HL} - \log \alpha_M$$

The data for a range of chelants with Cu and Ca is given below:

<u>Chelant</u>	<u>log Conditional Stability Constant (pH 10)</u>		
	<u>Cu</u>	<u>Ca</u>	<u>Ratio Cu/Ca</u>
EDDHA	21.04	4.97	4.23
EDDS	16.04	4.27	3.76
DTPMP	15.14	4.74	3.19
EDTMP	17.99	6.15	2.92
DTPA	18.78	10.13	1.85
HEDP	8.98	5.13	1.75
EDTA	16.37	10.24	1.60

The applicant has surprisingly found that levels as low as 0.25% by weight of chelants having a ratio $\frac{\log K_{CuL}}{\log K_{CaL}}$ (wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant between this chelant and Cu^{2+} and wherein $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant between this chelant and Ca^{2+} , both at pH 10) of at least 3.20 give good oxidative damage protection. This $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio should preferably be at least 3.30, more preferably at least 3.40, even more preferably at least 3.50 at pH 10. It is important to calculate this ratio at pH 10 because oxidizing compositions for treating hair usually have a pH of from 8 to 12. Using stability constants without taking into account the influence of the pH is a common mistake and will give misleading results for the purpose of identifying chelants that will prevent oxidative damage at low levels.

Hydrogen Peroxide Decomposition Ratio (%Loss)

It is preferred that the complexes formed by these preferred chelants efficiently inhibit the red-ox chemistry of Cu^{2+} . The ability of chelants to inhibit the red-ox chemistry of the chelated copper metal ion can be effectively compared using their Hydrogen Peroxide Decomposition Ratio (% Loss) as measured by

the Hydrogen Peroxide Decomposition Ratio Measurement Protocol described hereafter in the "EXPERIMENTALS" section.

The table below shows the Hydrogen Peroxide Decomposition Ratio (% Loss) for different chelants:

Chelant	Peroxide % at t=0	Peroxide % at t=30mn	% Loss
EDTA	3.576	3.573	0.1%
EDDS	3.150	3.104	1.5%
DTPMP	3.078	2.964	3.7%
MGDA	3.498	3.104	11.3%
HEDP	4.126	2.792	32.3%
No chelant	0.563	-	100%

5

MGDA is methylglycinediacetic acid and forms a pentadentate complex with Cu²⁺.

Chelants forming hexadentate type complexes with Cu²⁺ were found to adequately inhibit the red-ox chemistry of the metal ion ("hexadendate complex" means that the chelant forms six bonds with the chelated metal ion). Examples of chelants that form such complexes with Cu²⁺ are EDDS, HBED, EDTA and EDDHA. Forming such complexes efficiently prevents the chelated heavy metal ion from reacting with the molecule of the oxidizing agent, for example hydrogen peroxide.

As the table above shows, EDTA has a very good capacity at inhibiting the red-ox chemistry of copper. This was a very surprising finding for the inventors because experiments had shown that EDTA had very poor damage prevention properties in "real" conditions of use wherein the concentration of transition metal ion such as copper and alkaline-earth metal ion such as Ca²⁺ are high compared to lab-condition wherein the water is de-ionized for experiments. (see EXPERIMENTALS hereinbelow). The Applicant believes that this clearly shows

that the ratio $\frac{\log K_{CuL}}{\log K_{CaL}}$ at pH 10 is an essential parameter to use in order to determine the oxidative damage prevention efficiency of chelants in real conditions of use.

Without being bound by theory, it is believed that chelants act to chelate environmental and intrinsic heavy metal ions such as iron, manganese and copper. In the absence of chelants, these heavy metal ions react with hydrogen peroxide to give highly damaging species such as free radicals, which are 5 believed to be very harmful to the disulphide bonds of hair. It is believed that alkaline-earth metal ions such as Ca^{2+} compete with heavy metal ions to form complexes with the chelants, therefore chelants with a much higher affinity for Cu^{2+} than for Ca^{2+} will much more efficiently prevent oxidative damage than chelants with a lower relative affinity for Cu^{2+} . The Applicant believes that the 10 importance of measuring damage under real life conditions (i.e. at pH10 and with non-deionized water) was never recognized or foreseen until now.

Oxidizing agent

The compositions according to the present invention comprise or are used in combination with a composition that comprises at least one oxidizing agent. 15 Preferred oxidizing agents for use herein are water-soluble peroxygen oxidizing agents. "Water-soluble" as defined herein means that in standard condition at least 0.1g, preferably 1g, more preferably 10g of said oxidizing agent can be dissolved in 1 liter of deionized water. The oxidizing agents are valuable for the initial solubilisation and decolorisation of the melanin (bleaching) and accelerate 20 the polymerization of the oxidative dye precursors (oxidative dyeing) in the hair shaft.

Preferred water-soluble oxidizing agents are inorganic peroxygen materials capable of yielding hydrogen peroxide in an aqueous solution. Water-soluble peroxygen oxidizing agents are well known in the art and include 25 hydrogen peroxide, inorganic alkali metal peroxides such as sodium periodate and sodium peroxide and organic peroxides such as urea peroxide, melamine peroxide, and inorganic perhydrate salt bleaching compounds, such as the alkali metal salts of perborates, percarbonates, perphosphates, persilicates, persulphates and the like. These inorganic perhydrate salts may be incorporated 30 as monohydrates, tetrahydrates etc. Mixtures of two or more such oxidizing

agents can be used if desired. Preferred for use in the compositions according to the present invention is hydrogen peroxide.

In conventional dyeing and bleaching compositions, levels of peroxygen oxidizing agent are usually of from about 0.1% to about 7% by weight. Higher 5 levels, whilst giving good results in term of efficacy were until now not practical because of increased hair damage. The oxidative damage protection provided by the present invention makes it now possible to use oxidizing agent such as hydrogen peroxide in level up to 40% in the oxidizing composition. However, for safety reasons, level above 12% should be carefully investigated before being 10 used on human. Preferably, the level of the oxidizing agent in the oxidizing composition is of from about 0.5% to about 20% by weight, more preferably of from about 1% to about 15%. The compositions according to the present invention provide excellent gray coverage, vibrant colors and acceptable damage at level above about 7% (typically about 12%).

15 The weight ratio of oxidizing agent to oxidative damage inhibiting chelant (e.g. EDDS) is preferably in the range of from 50:1 to 1:50, preferably from 25:1 to 1:25, more preferably from 15:1 to 1:15, even more preferably of from 9:1 to 1:10.

Additional components

20 Moreover, it is also intended that the compositions of the present invention may be complex compositions, which in addition to the chelant and oxidizing agent comprise other components that may or may not be active ingredients. This includes, but is not limited to, buffering agents, hair dyeing agents such as oxidative dye precursors, non-oxidative dyes, thickeners, solvents, enzymes, 25 anionic, non ionic, amphoteric and cationic surfactants, conditioning agents, carriers, antioxidants (such as erythorbic acid, sodium metabisulphite, tocopherol acetate, tocopherol), stabilizers, perming actives, perfume, reducing agent (thiolactic acid), hair swelling agents and/or polymers. Some of these additional components are detailed hereafter.

It is preferred, however, that the composition according to the present invention should preferably be substantially free from sodium nonanoylbenzenesulfonate (NOBS), acetyltriethylcitrate (ATC), sodium (6-nonaamidocaproyl)oxybenzenesulfonate, peracetic and pernanoic acid since 5 they have a negative effect on the efficiency of bleaching and coloring and increase damage at a pH above 8. The composition should be substantially free from organic peroxyacid precursors and preformed organic peroxyacid, such as those defined in WO97/24106. The term substantially free as used herein means that the compositions according to the present invention should comprise less 10 than 1.5%, preferably less than 1%, more preferably less than 0.5%, even more preferably less than 0.1%, still more preferably 0% by weight of the composition of such compounds.

It is might be also preferred that the compositions of the present invention are substantially free of inorganic phosphate or phosphonate compounds since 15 they are usually non- or poorly biodegradable.

Finally, the compositions according to the present invention can be provided in any usual form, such as for example an aqueous composition, a powder, a gel or an oil-in-water emulsion. Preferred media for the compositions according to the present invention are thickened solutions comprising a salt-tolerant thickener or oil-in-water emulsions.

pH buffering agents

The compositions according to the present invention preferably further comprise a pH buffering agent. The pH of the composition is preferably of from about 8 to about 12, more preferably of from about 9 to about 11, even more 25 preferably of from about 9.5 to about 10.5. Suitable buffering agents are well known in the art and include for example ammonia/ammonium acetate mixture, monoethanolamine (MEA), tetrasodium pyrophosphate, isopropanolamine, benzoic acid.

Oxidative hair dye precursors

Oxidative dyeing compositions according to the present invention further comprise oxidative hair dye precursors (also known as primary intermediates) that will deliver a variety of hair colors to the hair. These small molecules are activated by the oxidizing agent and react with further molecules to form a larger colored complex in the hair shaft.

The precursors can be used alone or in combination with other precursors, and one or more can be used in combination with one or more couplers. Couplers (also known as color modifiers or secondary intermediates) are generally colorless molecules that can form colors in the presence of activated precursors, and are used with other precursors or couplers to generate specific color effects or to stabilize the color.

The choice of precursors and couplers will be determined by the color, shade and intensity of coloration that is desired. The precursors and couplers can be used herein, singly or in combination, to provide dyes having a variety of shades ranging from ash blonde to black.

These compounds are well known in the art, and include aromatic diamines, aminophenols and their derivatives (a representative but not exhaustive list of oxidation dye precursor can be found in Sagarin, "Cosmetic Science and Technology", "Interscience, Special Edn. Vol. 2 pages 308 to 310). It is to be understood that the precursors detailed below are only by way of example and are not intended to limit the compositions and processes herein. These are: pyrogallol, resorcinol, p-toluenediamine, p-phenylenediamine, o-phenylenediamine, m-phenylenediamine, o-aminophenol, p-aminophenol, 4-amino-2-nitrophenol, nitro-p-phenylenediamine, N-phenyl-p-phenylenediamine, m-aminophenol, 2-amino-3-hydroxypyridine, 1-naphthol, N,N bis (2-hydroxyethyl)p-phenylenediamine, 4-amino-2-hydroxytoluene, 1,5-dihydroxynaphthalene, 2-methyl resorcinol and 2,4-diaminoanisole. These can be used in the molecular form or in the form of peroxide-compatible salts.

Hair dye compositions will generally comprise from about 0.001% to about 10% of oxidative dye precursors and couplers. For example compositions providing low intensity dyeing such as natural blond to light brown hair shades

generally comprise from about 0.001% to about 5%, preferably from about 0.1% to about 2%, more preferably from about 0.2% to about 1% by weight of dyeing composition of precursors and couplers.

The composition of the present invention may optionally further comprise
5 at least about 0.1% of thickeners. Thickeners are preferably comprised in amount sufficient to provide the composition with a viscosity of from about 1 Pa.s to 10 Pa.s (1,000 to 10,000 cP) at 26°C in order to provide a composition that can be readily applied to the hair without dripping.

A non exhaustive list of commonly used thickeners are cetearyl alcohol,
10 oleyl alcohol, cocamide MIPA, glycol esters (ex. distearate), silica dimethyl silylate, carbomer, linoleic acid, palmitic acid, stearic acid, and PEG 150/Stearyl/SMDI copolymer.

Preferred for use herein are salt tolerant thickeners. Salt-tolerant thickeners are functionally defined herein as compounds that increases the
15 viscosity of an aqueous composition consisting of 3.8% DTPMP (tetrasodium salt) and 1.95% NH₃ to at least 1 Pa.s (1,000 cP) when incorporated at levels of 2% by weight as measured at 26.7°C. The viscosity can be measured with a Brookfield viscometer DVII, using S41 spindles for samples under 10 Pa.s (10,000 cP) and spindle S52 for samples over 10 Pa.s (10,000 cP) (available
20 from Brookfield), with a speed rating of 1 revolution per minute and samples sizes of 2ml (for S41 spindle) or 0.5 ml (for S52 spindle).

A non exclusive list of suitable salt tolerant thickeners for use herein include xanthan, guar, hydroxypropyl guar, scleroglucan, methyl cellulose, ethyl cellulose (commercially available as Aquacote®), hydroxyethyl cellulose
25 (Natrosol®), carboxymethyl cellulose, hydroxypropylmethyl cellulose, microcrystalline cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose (Klucel®), hydroxyethyl ethyl cellulose, cetyl hydroxyethyl cellulose (Natrosol® Plus 330), N-vinylpyrrolidone (Povidone®), Acrylates / Ceteth-20 Itaconate Copolymer (Structure® 3001), hydroxypropyl starch phosphate (Structure® ZEA), polyethoxylated urethanes or polycarbamyl polyglycol ester (e.g. PEG-
30 150/Decyl/SMDI copolymer = Aculyn® 44, PEG-150/Stearyl/SMDI copolymer =

Aculyn 46®), trihydroxystearin (Thixcin®) acrylates copolymer (e.g. Aculyn® 33) or hydrophobically modified acrylate copolymers (e.g. Acrylates / Steareth-20 Methacrylate Copolymer = Aculyn® 22).

Fatty alcohols have thickening properties and can be used in the compositions of the present invention. Fatty alcohols are however not salt-tolerant thickeners according to the above definition. A mixture of 2% cetyl and stearyl alcohol has for example a viscosity of less than about 0.7 Pa.s (700 cP) as measured at 26°C with a Brookfield viscometer in the conditions disclosed hereabove.

10

Conditioning agent

The compositions of the present invention comprise or are used in combination with a composition comprising a conditioning agent. Conditioning agents suitable for use herein are selected from silicone materials, fatty alcohols, polymeric resins, polyol carboxylic acid esters, cationic polymers, cationic surfactant, insoluble oils and oil derived materials and mixtures thereof. Additional materials include mineral oils and other oils such as glycerin and sorbitol.

The conditioning agent will generally be used at levels of from about 0.05% to about 20% by weight of the composition, preferably of from about 0.1% to about 15%, more preferably of from about 0.2% to about 10%, even more preferably of from about 0.2% to about 2%. The minimum level that is used in a particular composition should be effective to provide a conditioning benefit. The maximum level that can be used is not limited by theory, but rather by practicality. It is generally unnecessary and expensive to use levels in excess of about 10% and, depending on the type of agent (polymeric conditioners being most prone), such high levels can cause an undesirable weighting down of the hair.

When used as post-treatment immediately after the oxidizing composition has been applied and optionally rinsed off, the levels of conditioner in the post

treatment composition are similar as those disclosed above, but by weight of the composition applied as a post-treatment.

Silicone Materials

Suitable silicone conditioning agents for use herein are nonvolatile and
5 insoluble in the shampoo composition and will intermix in the shampoo
composition so as to be in the form of an emulsion, i.e., a separate,
discontinuous phase of dispersed, insoluble droplets. These droplets are
suspended with a suspending agent, numerous, non-exclusive suitable
examples of which are described below. This dispersed silicone conditioning
10 component will comprise a silicone fluid hair conditioning agent such as a
silicone fluid and can also comprise other ingredients, such as a silicone resin to
enhance silicone fluid deposition efficiency or, for example, enhance glossiness
of the hair (especially when high refractive index (e.g. above about 1.46) silicone
conditioning agents are used (e.g. highly phenylated silicones)).

15 The silicone conditioning agent phase may comprise volatile silicone
components. Typically, if volatile silicones are present, it will be incidental to
their use as a solvent or carrier for commercially available forms of nonvolatile
silicone materials ingredients, such as silicone gums and resins.

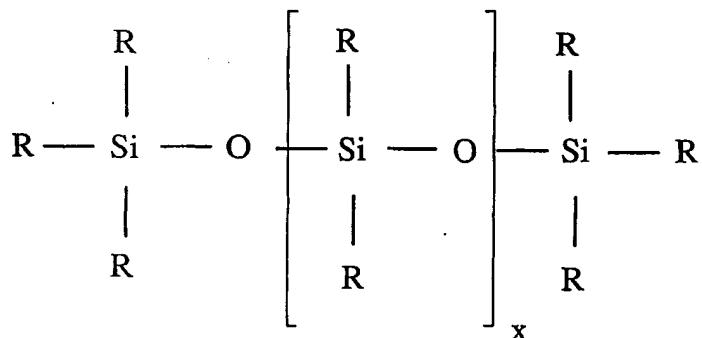
The silicone conditioning agent component for use herein will preferably
20 have viscosity of from about 20 to about 2,000,000 centistokes at 25°C, more
preferably from about 1,000 to about 1,800,000, even more preferably from
about 50,000 to about 1,500,000, most preferably from about 100,000 to about
1,500,000.. The viscosity can be measured by means of a glass capillary
viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July
25 20, 1970.

The silicone conditioning agent component will generally be used in the
shampoo compositions hereof at levels of from about 0.05% to about 10% by
weight of the composition, preferably from about 0.1% to about 8%, more
preferably from about 0.1% to about 5%, most preferably from about 0.1% to
30 about 3%. The minimum level that is used in a particular composition should be

effective to provide a conditioning benefit. The maximum level that can be used is not limited by theory, but rather by practicality. It is generally unnecessary and expensive to use levels in excess of about 8%, although higher levels can be used if desired.

5 One type of silicone fluid that can be used herein is a silicone oil. The term "silicone oil" shall mean flowable silicone materials having a viscosity of less than 1,000,000 centistokes at 25°C. Generally, the viscosity of the fluid will be between about 5 and 1,000,000 centistokes at 25°C, preferably between about 10 and about 100,000. Suitable silicone oils include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other insoluble, nonvolatile silicone fluids having hair conditioning properties can also be used. More particularly silicone oils hereof include polyalkyl or polyaryl siloxanes having the general formula (XII):

10



15 wherein R is aliphatic, preferably alkyl or alkenyl, or aryl, R can be substituted or unsubstituted, and x is an integer from 1 to about 8,000. Suitable unsubstituted R groups include alkoxy, aryloxy, alkaryl, arylalkyl, arylalkenyl, alkamino, and ether-substituted, hydroxyl-substituted, and halogen-substituted aliphatic and aryl groups. Suitable R groups also include cationic amines and
20 quaternary ammonium groups.

The aliphatic or aryl groups substituted on the siloxane chain may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair and / or skin, are compatible with the other components of the

composition, are chemically stable under normal use and storage conditions, are insoluble in the composition, and are capable of being deposited on and, of conditioning, the hair and / or skin. The two R groups on the silicon atom of each monomeric silicone unit may represent the same group or different groups.

5 Preferably, the two R groups represent the same group.

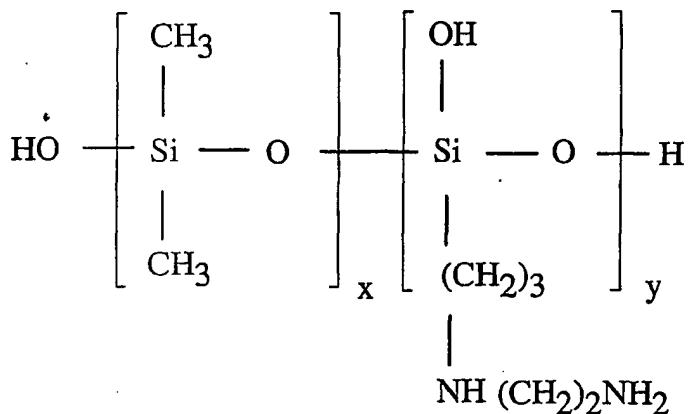
Preferred alkyl and alkenyl substituents are C₁-C₅ alkyls and alkenyls, more preferably from C₁-C₄, most preferably from C₁-C₂. The aliphatic portions of other alkyl-, alkenyl-, or alkynyl-containing groups (such as alkoxy, alkaryl, and alkamino) can be straight or branched chains and preferably have from one to 10 five carbon atoms, more preferably from one to four carbon atoms, even more preferably from one to three carbon atoms, most preferably from one to two carbon atoms. As discussed above, the R substituents hereof can also contain amino functionalities, e.g. alkamino groups, which can be primary, secondary or tertiary amines or quaternary ammonium. These include mono-, di- and tri-15 alkylamino and alkoxyamino groups wherein the aliphatic portion chain length is preferably as described above. The R substituents can also be substituted with other groups, such as halogens (e.g. chloride, fluoride, and bromide), halogenated aliphatic or aryl groups, and hydroxy (e.g. hydroxy substituted aliphatic groups). Suitable halogenated R groups could include, for example, tri-20 halogenated (preferably fluoro) alkyl groups such as -R¹-C(F)₃, wherein R¹ is C₁-C₃ alkyl. Examples of such polysiloxanes include polymethyl -3,3,3 trifluoropropylsiloxane.

The nonvolatile polyalkylsiloxane fluids that may be used include, for example, polydimethylsiloxanes. These siloxanes are available, for example, 25 from the General Electric Company in their Viscasil R and SF 96 series, and from Dow Corning in their Dow Corning 200 series. Also suitable for use herein is Dow Corning DC 1664 (TN) 60,000 cstk polydimethyl siloxane with 300nm particle size which is preferably used in combination with a deposition aid. Polydimethyl silicone is also known as dimethicone oil. Other suitable R groups 30 include methyl, methoxy, ethoxy, propoxy, and aryloxy. The three R groups on the end caps of the silicone may also represent the same or different groups.

Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

5 The polyalkylaryl siloxane fluids that may be used, also include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

The polyether siloxane copolymers that may be used include, for example,
10 10 a polypropylene oxide modified polydimethylsiloxane (e.g., Dow Corning DC-1248) although ethylene oxide or mixtures of ethylene oxide and propylene oxide may also be used. The ethylene oxide and polypropylene oxide level must be sufficiently low to prevent solubility in water and the composition hereof.
Alkylamino substituted silicones that can be used herein include those of the
15 formula :



in which x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

20 Cationic silicone fluids which can be used in the present compositions include those that correspond to the formula:



in which G is chosen from the group consisting of hydrogen, phenyl, OH, C₁-C₈ alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R₁ is a monovalent radical of formula C_qH_{2q}L in which q is an integer from 2 to 8 and L is chosen from the groups:

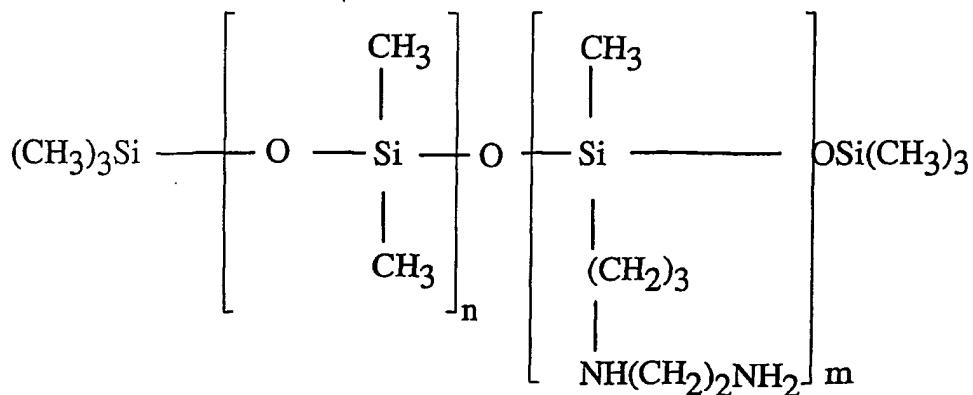
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- N(R₂)CH₂-CH₂-N(R₂)₂
- N(R₂)₂
- N+(R₂)₃A⁻
- N(R₂)CH₂-CH₂-N+R₂H₂A⁻

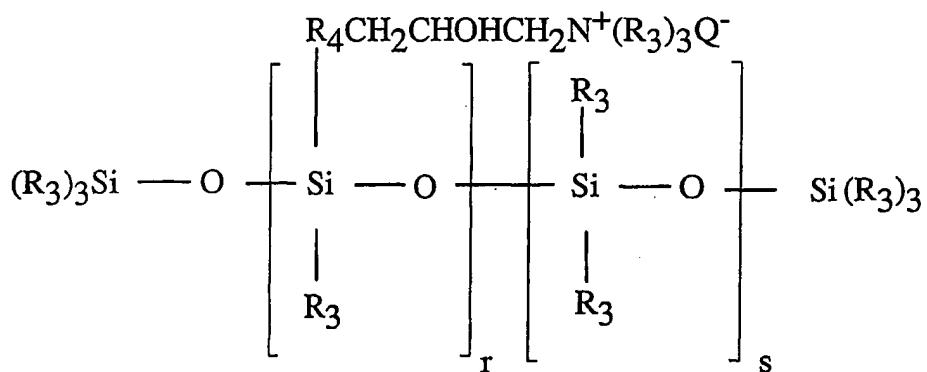
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in which R₂ is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A⁻ denotes a halide ion.

An especially preferred cationic silicone corresponding to formula immediately above is the polymer known as "trimethylsilylamodimethicone", of formula:



Other silicone cationic polymers which can be used in the present compositions correspond to the formula:



5

in which R_3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, and more especially an alkyl or alkenyl radical such as methyl; R_4 denotes a hydrocarbon radical such as, preferably a $\text{C}_1\text{-C}_{18}$ alkylene radical or a $\text{C}_1\text{-C}_{18}$, and preferably $\text{C}_1\text{-C}_8$, alkyleneoxy radical; Q is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. These compounds are described in greater detail in US-A-4,185,017. A polymer of this class which is especially preferred is that sold by UNION CARBIDE under the name "UCAR SILICONE ALE 56"(TN).

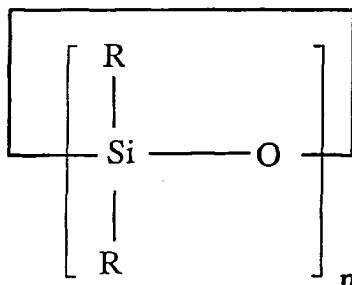
15 Another silicone fluid that can be especially useful in the silicone conditioning agents is insoluble silicone gum. The term "silicone gum", as used herein, means polyorganosiloxane materials having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. Silicone gums are described by Petrarch and others including US-A-4,152,416, Spitzer et al., issued May 1, 1979 and
 20 Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include

polydimethylsiloxane, (polydimethylsiloxane) (methylvinylsiloxane) copolymer, poly(dimethylsiloxane) (diphenyl siloxane)(methylvinylsiloxane) copolymer and mixtures thereof.

Preferably the silicone hair and /or skin conditioning agent comprises a
 5 mixture of a polydimethylsiloxane gum, having a viscosity greater than about 1,000,000 centistokes and polydimethylsiloxane oil having a viscosity of from about 10 centistokes to about 100,000 centistokes, wherein the ratio of gum to fluid is from about 30:70 to about 70:30, preferably from about 40:60 to about 60:40.

10 Another category of nonvolatile, insoluble silicone fluid conditioning agents are high refractive index silicones, having a refractive index of at least about 1.46, preferably at least about 1.48, more preferably at least about 1.52, most preferably at least about 1.55. Although not intended to necessarily be limiting, the refractive index of the polysiloxane fluid will generally be less than about
 15 1.70, typically less than about 1.60. Polysiloxane "fluid" includes oils as well as gums.

The high refractive index polysiloxane fluid suitable for purposes hereof includes those represented by general Formula (XII) above, as well as cyclic polysiloxanes such as those represented by the formula:



20

wherein R is as defined above, n is from about 3 to about 7, preferably from 3 to 5. The high refractive index polysiloxane fluids hereof contain a sufficient amount of aryl-containing R substituents to increase the refractive index to the desired level, which is described above. In addition, R and n must be selected so that the material is nonvolatile, as defined above.
 25

Aryl-containing substituents contain alicyclic and heterocyclic five and six membered aryl rings, and substituents containing fused five or six membered rings. The aryl rings themselves can be substituted or unsubstituted. Substituents include aliphatic substituents, and can also include alkoxy substituents, acyl substituents, ketones, halogens (e.g., Cl and Br), amines, etc.

5 Exemplary aryl-containing groups include substituted and unsubstituted arenes, such as phenyl, and phenyl derivatives such as phenyls with C₁-C₅ alkyl or alkenyl substituents, e.g., allylphenyl, methyl phenyl and ethyl phenyl, vinyl phenyls such as styrenyl, and phenyl alkynes (e.g. phenyl C₂-C₄ alkynes).

10 Heterocyclic aryl groups include substituents derived from furan, imidazole, pyrrole, pyridine, etc. Fused aryl ring substituents include, for example, naphthalene, coumarin, and purine.

In general, the high refractive index polysiloxane fluids hereof will have a degree of aryl-containing substituents of at least about 15%, preferably at least 15 about 20%, more preferably at least about 25%, even more preferably at least about 35%, most preferably at least about 50%. Typically, although it is not intended to necessarily limit the invention, the degree of aryl substitution will be less than about 90%, more generally less than about 85%, preferably from about 55% to about 80%.

20 These polysiloxane fluids are also characterised by relatively high surface tensions as a result of their aryl substitution. In general, the polysiloxane fluids hereof will have a surface tension of at least about 24 dynes/cm², typically at least about 27 dynes/cm². Surface tension, for purposes hereof, is measured by a de Nouy ring tensiometer according to Dow Corning Corporate Test Method 25 CTM 0461, November 23, 1971. Changes in surface tension can be measured according to the above test method or according to ASTM Method D 1331.

The preferred high refractive index polysiloxane fluids hereof will have a combination of phenyl or phenyl derivative substituents (preferably phenyl), with alkyl substituents, preferably C₁-C₄ alkyl (most preferably methyl), hydroxy, C₁-30 C₄ alkylamino (especially -R¹NHR²NH₂ where each R¹ and R² independently is a C₁-C₃ alkyl, alkenyl, and/or alkoxy. High refractive index polysiloxane are

available commercially from Dow Corning Corporation (Midland, Michigan, U.S.A.) Huls America (Piscataway, New Jersey, U.S.A.), and General Electric Silicones (Waterford, New York, U.S.A.).

It is preferred to utilise high refractive index silicones in solution with a spreading agent, such as a silicone resin or a surfactant, to reduce the surface tension by a sufficient amount to enhance spreading and thereby enhance glossiness (subsequent to drying) of hair treated with the composition. In general, a sufficient amount of the spreading agent to reduce the surface tension of the high refractive index polysiloxane fluid by at least about 5%, preferably at least about 10%, more preferably at least about 15%, even more preferably at least about 20%, most preferably at least about 25%. Reductions in surface tension of the polysiloxane fluid/spreading agent mixture can provide improved shine enhancement of the hair.

Also, the spreading agent will preferably reduce the surface tension by at least about 2 dynes/cm², preferably at least about 3 dynes/cm², even more preferably at least about 4 dynes/cm², most preferably at least about 5 dynes/cm².

The surface tension of the mixture of the polysiloxane fluid and the spreading agent, at the proportions present in the final product, is preferably 30 dynes/cm² or less, more preferably about 28 dynes/cm² or less most preferably about 25 dynes/cm² or less. Typically the surface tension will be in the range of from about 15 to about 30, more typically from about 18 to about 28, and most generally from about 20 to about 25 dynes/cm².

The weight ratio of the highly arylated polysiloxane fluid to the spreading agent will, in general, be between about 1000:1 and about 1:1, preferably between about 100:1 and about 2:1, more preferably between about 50:1 and about 2:1, most preferably from about 25:1 to about 2:1. When fluorinated surfactants are used, particularly high polysiloxane: spreading agent ratios may be effective due to the efficiency of these surfactants. Thus is contemplated that ratios significantly above 1000:1 may be used.

References disclosing suitable silicone fluids include US-A-2,826,551, Geen; US-A-3,964,500, Drakoff, issued June 22, 1976; US-A-4,364,837, Pader; and GB-A-849,433, Woolston and 'Silicon Compounds' distributed by Petrarch Systems, Inc., 1984 which provides an extensive (though not exclusive) listing of
5 suitable silicone fluids.

An optional ingredient that can be included in the silicone hair and /or skin conditioning agent is silicone resin. Silicone resins are highly cross linked polymeric siloxane systems. The cross linking is introduced through the incorporation of trifunctional and tetrafunctional silanes with monofunctional or
10 difunctional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of cross linking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units (and hence, a sufficient
15 level of cross linking) such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of cross linking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms
20 is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methyl-phenyl-, monovinyl-, and methylvinyl-chlorosilanes, and tetrachlorosilane, with the methyl-substituted silanes being most commonly utilised. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially
25 available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Background material on silicones including sections discussing silicone fluids, gums, and
30 resins, as well as manufacture of silicones, can be found in Encyclopaedia of

Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as "MDTQ" nomenclature. Under this system, the silicone is described according to presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the monofunctional unit $(CH_3)_3SiO_{0.5}$; D denotes the difunctional unit $(CH_3)_2SiO$; T denotes the trifunctional unit $(CH_3)SiO_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyls, amines, hydroxyls, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone (or an average thereof) or as specifically indicated ratios in combination with molecular weight complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of cross linking. As discussed before, however, the overall level of cross linking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MDT and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

The weight ratio of the nonvolatile silicone fluid, having refractive index below 1.46, to the silicone resin component, when used, is preferably from about 4:1 to about 400:1, preferably this ratio is from about 9:1 to about 200:1, more preferably from about 19:1 to about 100:1, particularly when the silicone fluid component is a polydimethylsiloxane fluid or a mixture of polydimethylsiloxane fluid and polydimethylsiloxane gum as described above. Insofar as the silicone

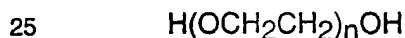
resin forms a part of the same phase in the compositions hereof as the silicone fluid, i.e. the conditioning active, the sum of the fluid and resin should be included in determining the level of conditioning agent in the composition.

Fatty Alcohols

5 Fatty alcohols suitable for use as conditioning agents for the hair and /or skin herein have the general formula, R-OH, wherein R is a straight or branched chain hydrocarbyl, preferably straight chain containing from about 8 to about 22 carbon atoms, preferably from about 12 to about 18 carbon atoms. It should be understood that the definition of any particular carbon chain length, say, C₁₆ is
10 an average value and as such may contain certain proportions of both higher and lower carbon chain lengths as a direct function of its synthesis. Suitable fatty alcohols for use herein include cetyl alcohol, available under the trade names CO-1695 (TN) from Procter and Gamble Ltd. and Laurex 16 (TN) from Albright and Wilson Ltd.; and stearyl alcohol, available under the trade names
15 CO 1895 (TN) from Procter and Gamble Ltd. and Laurex 18 (TN) from Albright and Wilson Ltd.

Water-Soluble Resins

Additional conditioning agents suitable for use herein are water-soluble resins having molecular weights in the range of from about 8,000 to about
20 2,000,000. Water-soluble, as defined herein means, a material that is sufficiently soluble in water to form a substantially clear solution, to the naked eye, at a concentration of about 0.1% by weight of the material in water at about 25°C. Water-soluble resins useful as conditioning agents herein are nonionic polyethylene glycol polymers having the general formula:



wherein n is an average value of ethoxylation in the range of from about 1000 to about 25,000, preferably from about 10,000 to about 20,000. Nonionic resins suitable for use herein include narrow molecular weight distribution PEG 14M, available under the trade name Polyox WSRN 3000 (TN) from Amerchol

and broad molecular weight PEG 2M available under the trade name Polyox WSRN 10 (TN) from Amerchol.

Polyol Carboxylic Acid Esters

Suitable for use herein as conditioning agents are liquid polyol carboxylic acid esters. These polyol esters are derived from a polyol with one or more carboxylic acids. In other words, these esters contain a moiety derived from a polyol and one or more moieties derived from a carboxylic acid. These carboxylic acid esters can also be described as liquid polyol fatty acid esters, because the terms carboxylic acid and fatty acid are often used interchangeably by those skilled in the art. As used herein, the term liquid, means a fluid which is visibly flowable (to the naked eye) under ambient conditions (about 1 atmosphere of pressure at about 25°C).

The liquid polyol polyesters suitable for use herein comprise certain polyols, especially sugars, sugar alcohols or sugar ethers, esterified with at least two fatty acid groups. The polyol starting material, however, preferably has at least about four esterifiable hydroxyl groups. Examples of preferred polyols are sugars, including monosaccharides and disaccharides, sugar alcohols or sugar ethers. Examples of monosaccharides containing four hydroxyl groups are xylose and arabinose and the sugar alcohol derived from xylose, which has five hydroxyl groups, i.e., xylitol. The monosaccharide, erythrose, is also suitable in the practice of this invention since it contains three hydroxyl groups, as is the sugar alcohol derived from erythrose, i.e., erythritol, which contains four hydroxyl groups. Suitable five hydroxyl group-containing monosaccharides are galactose, fructose, and sorbose. Sugar alcohols containing six hydroxyl groups derived from the hydrolysis products of sucrose, as well as glucose and sorbose, e.g., sorbitol, are also suitable. Examples of disaccharide polyols which can be used include maltose, lactose, and sucrose, all of which contain eight hydroxyl groups. In addition, sugar ethers are also suitable for the practise of this invention, such as, sorbitan.

The polyols used in such liquid polyol esters preferably have from about 4 to about 12, more preferably from about 4 to about 11, and most preferably from about 4 to about 8 hydroxyl groups. Preferred polyols for preparing the polyesters suitable for use herein are selected from the group consisting of 5 erythritol, xylitol, sorbitol, glucose, and sucrose. Sucrose is especially preferred.

The preferred polyol starting material having at least four hydroxyl groups must be esterified on at least two of the hydroxyl groups with a fatty acid containing from about 8 to about 22 carbon atoms, preferably from about 8 to about 14 carbon atoms. Examples of such fatty acids include caprylic, capric, 10 lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, ricinoleic, linoleic, linolenic, eleostearic, arachidic, arachidonic, behenic, and erucic acids. The fatty acids can be derived from naturally occurring or synthetic fatty acids; they can be saturated or unsaturated, including positional and geometrical isomers. However, in order to provide liquid polyesters of the type suitable for use herein, 15 at least about half of the fatty acid incorporated into the polyester molecule must be unsaturated fatty acids, saturated short chain fatty acids, or mixtures thereof.

The liquid polyol fatty acid polyesters suitable for use as conditioning agents herein must contain at least two fatty acid ester groups. It is not necessary that all of the hydroxyl groups of the polyol be esterified with fatty 20 acids, but it is preferable that the polyester contain no more than two unesterified hydroxyl groups. Most preferably, substantially all of the hydroxyl groups of the polyol are esterified with fatty acids, i.e., the polyol moiety is substantially completely esterified. The fatty acids esterified to the polyol molecule can be the same or mixed, but as noted above, a substantial amount of the unsaturated 25 acid ester groups and/or saturated short chain acid ester groups must be present to provide liquidity.

To illustrate the above points, a sucrose di-fatty acid ester would be suitable, but is not preferred because it has more than two unesterified hydroxyl groups. A sucrose hexa-fatty acid ester would be preferred because it has no 30 more than two unesterified hydroxyl groups. Highly preferred compounds in

which all the hydroxyl groups are esterified with fatty acids include the liquid sucrose octa-substituted fatty acid esters.

The following are non-limiting examples of specific liquid polyol fatty acid polyesters containing at least two fatty acid ester groups suitable for use in the present invention: glucose dioleate, the glucose diesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose diesters of mixed soybean oil or cotton seed oil fatty acids, the galactose diesters of oleic acid, the arabinose diesters of linoleic acid, xylose dilinoleate, sorbitol dioleate, sucrose dioleate, glucose trioleate, the glucose triesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose triesters of mixed soybean oil or cotton seed oil fatty acids, the galactose triesters of oleic acid, the arabinose triesters of linoleic acid, xylose trilinoleate, sorbitol trioleate, sucrose trioleate, glucose tetraoleate, the glucose tetraesters of soybean oil or cotton seed oil fatty acids (unsaturated), the mannose tetraesters of mixed soybean oil or cotton seed oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil or cotton seed oil fatty acids, xylitol pentaoleate, sucrose tetraoleate, sucrose pentaoleate, sucrose hexaoleate, sucrose hepatoleate, sucrose octaoleate, and mixtures thereof.

The preferred liquid polyol polyesters of the present invention have complete melting points below about 30°C, preferably below about 27.5°C, and more preferably below about 25°C. Complete melting points reported herein are measured by Differential Scanning Calorimetry (DSC). The term "complete melting point", as used herein means a melting point as measured by the well-known technique of Differential Scanning Calorimetry (DSC). The complete melting point is the temperature at the intersection of the baseline, i.e. the specific heat line, with the line tangent to the trailing edge of the endothermic peak. Typically a scanning temperature of 5°C/minute is used in the present invention in measuring the complete melting points. A technique for measuring complete melting points is more fully described in US-A-5,306,514, to Letton et al., issued April 26, 1994.

Exemplary liquid polyol carboxylic acid esters suitable for use herein are sucrose polysoyate or sucrose polycottonseedoate available from Procter and Gamble.

The polyol fatty acid polyesters suitable for use herein can be prepared by

5 a variety of methods well known to those skilled in the art. These methods include: transesterification of the polyol with methyl, ethyl or glycerol fatty acid esters using a variety of catalysts; acylation of the polyol with a fatty acid chloride; acylation of the polyol with a fatty acid anhydride; and acylation of the polyol with a fatty acid, per se. See US-A-3,463,699, to Rizzi, issued June 15,

10 1976; and US-A-4,517,360 and 4,518,772 to Volpenhein issued 1985. The liquid polyol carboxylic acid conditioning agents suitable for use herein are biodegradable.

Cationic Polymers

Suitable cationic polymers for use herein will generally have a weight

15 average molecular weight which is at least about 200,000, typically at least about 400,000, and less than about 10 million. Preferably, the molecular weight is from about 400,000 to about 5 million, more preferably about 800,000 to about 2 million. The cationic polymers will have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof.

20 The cationic charge density is preferably at least about 0.3 meq/gram, more preferably at least about 0.6 meq/gram, even more preferably at least about 1.0 meq/gram, most preferably at least about 1.2 meq/gram. The cationic charge density in general will be about 4 meq/gram or less, more generally about 3.0 meq/gram or less. Cationic charge density of the cationic polymer can be

25 determined according to the Kjeldahl Method.

Those skilled in the art will recognize that the charge density of amino-containing polymers in the final product may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not intended to be exhaustive.

5 The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer 10 monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc. , Washington, D.C. 1 1982).

Suitable cationic polymers include, for example, copolymers of 15 vinylmonomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkylacrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-C3 20 alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the shampoo. In general, 25 secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by 30 reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably

a C₁ -C₇ alkyl, more preferably a C₁-C₃ alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinylpyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁-C₃ alkyls, more preferably C₁ and C₂ alkyls.

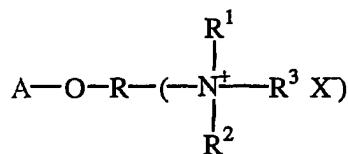
Suitable amine-substituted vinyl monomers for use herein included dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkylacrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁ -C₇ hydrocarbyls, more preferably C₁ -C₃, alkyls.

The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example, copolymers of 1-vinyl pyrrolidone and 1-vinyl methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT trademark (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from [SP Corporation (Wayne, NJ, USA) under the GAFQUAT trademark (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammoniumchloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in

the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference. Other cationic 5 polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives. Other cationic polymers suitable for use herein are copolymers of dimethyldiallyl ammonium chloride and acrylic acid (Polyquaternium 22).

Suitable cationic polymers are disclosed in WO9632919 p.17-21, 10 incorporated herein by reference. Examples of cationic polysaccharide polymer materials suitable for use herein include those of the formula:



wherein:

A is an anhydroglucose residual group, such as a starch or cellulose 15 anhydroglucose residual,

R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,

R¹, R², and R³ independently are alkyl, aryl, alkyl, aryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 20 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and

X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in 25 their Polymer JRTN, LRTN, KG^TN and LK^TN series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to

in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200 (or Quatrisoft).

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their JaguarS series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein). Especially preferred cationic polymers include Polyquaternium 10.

Suitable cationic cellulosic polymers for use herein have a molecular weight ranging from about 400,000 to about 1,500,000, preferably from about 500,000 to about 1,500,000 and most preferably from about 800,000 to about 1,200,000 and a charge density of from about 0.6 to about 3 meq./gr, preferably from about 0.7 to about 2.0 meq/gr. and most preferably from about 0.9 to about 1.5 meq/gr. Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR and LR series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10.

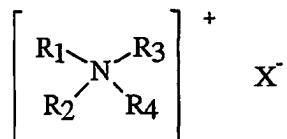
The water soluble cationic described herein are either soluble in the shampoo composition, or preferably are soluble in a complex coacervate phase in the shampoo composition formed by the cationic polymer and the anionic surfactant described herein before. Complex coacervates of the cationic polymer can also be formed with other optional anionic components of the shampoo composition.

Cationic surfactants

Cationic surfactants useful in compositions of the present invention contain amino or quaternary ammonium hydrophilic moieties which are positively charged when dissolved in the aqueous composition of the present invention.

Cationic surfactants containing quaternary ammonium moieties and silicone moieties can also be employed. Cationic surfactants among those useful herein are disclosed in the following documents, all incorporated by reference herein: M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1979); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591, Hilfer, issued November 3, 1964; U.S. Patent 3,929,678, Laughlin, et al., issued December 30, 1975; U.S. Patent 3,959,461, Bailey, et al., issued May 25, 1976; and U.S. Patent 4,387,090, Bolich, Jr., issued June 7, 1983.

10 Among the quaternary ammonium-containing cationic surfactant materials useful herein are those of the general formula:



wherein R₁-R₄ are independently an aliphatic group of from about 1 to about 22 carbon atoms, aryl, or an alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, or 15 alkylaryl group having from about 1 to about 22 carbon atoms; and X is an anion selected from halogen (especially chlorine), acetate, phosphate, nitrate and alkylsulfate (preferably C₁-C₃ alkyl) radicals. The aliphatic groups may contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 20 carbons, or higher, can be saturated or unsaturated.

Quaternary ammonium salts include dialkyldimethyl-ammonium chlorides, wherein the alkyl groups have from about 12 to about 22 carbon atoms and are derived from long-chain fatty acids, such as hydrogenated tallow fatty acid (tallow fatty acids yield quaternary compounds wherein R₁ and R₂ have predominately 25 from 16 to 18 carbon atoms). Other cationic surfactants include those wherein at least one of the R₁-R₄ radicals contains one or more hydrophilic moieties selected from alkoxy (preferably C₁-C₃ alkoxy), polyoxyalkylene (Preferably C₁-C₃ polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations

thereof. Optionally, the cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties in the R₁-R₄ groups. For purposes herein, each hydrophilic amido, alkoxy, hydroxyalkyl, alkylester, alkylamido or other unit is considered to be a distinct nonionic hydrophile moiety.

5 Other quaternary ammonium salts useful herein are diquaternaryammonium salts, such as tallow propane diammonium dichloride.

Salts of primary, secondary and tertiary fatty amines are also suitable cationic surfactant materials. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and may be substituted or 10 unsubstituted. Such amines, useful herein, include stearamido propyldimethyl amine, diethyl amino ethyl stearamide, dimethyl stearamine, dimethyl soyamine, soyamine, myristyl amine, tridecyl amine, ethylste arylamine, N-tallowpropane diamine, ethoxylated (5 moles E.O.) stearylamine, dihydroxy ethyl stearylamine, and arachidylbehenylamine.

15 Suitable amine salts include the halogen, acetate, phosphate, nitrate, citrate, lactate and alkyl sulfate salts. Such salts include stearylaminehydrochloride, soyamine chloride, stearylamine formate, N-tallowpropanediamine dichloride and stearamidopropyl dimethylamine citrate. Cationicamine surfactants included among those useful in the present invention 20 are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981,incorporated by reference herein.

Insoluble Oils

The compositions of the invention may also include an insoluble perfume or cosmetic oil or wax or a mixture thereof as conditioning agents at a level of up 25 to about 10%, preferably up to about 3% by weight. Insoluble oil or wax as defined herein means, the oil or wax is insoluble, in the sense of being insoluble in the product matrix at a temperature of 25°C.

Suitable insoluble cosmetic oils and waxes for use herein as conditioning agents include: C₁-C₂₄ esters of C₈-C₃₀ fatty acids such as isopropyl myristate, 30 myristyl myristate and cetyl ricinoleate, C₈-C₃₀ esters of benzoic acid, beeswax,

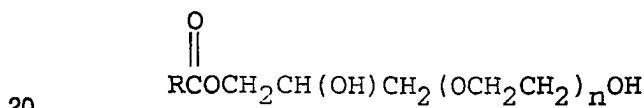
saturated and unsaturated fatty alcohols such as behenyl alcohol, hydrocarbons such as mineral oils, petrolatum squalane and squalene, polybutene, fatty sorbitan esters (see US-A-3,988,255, Seiden, issued October 26th 1976), lanolin and oil-like lanolin derivatives, animal and vegetable triglycerides such as

5 almond oil, peanut oil, wheat germ oil, rice bran oil, linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soyabean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil, and C₁-C₂₄ esters of dimer and trimer acids such as

10 diisopropyl dimerate, diisostearylmalate, diisostearyldimerate and triisostearyltrimerate and mixtures thereof.

Oil Derived Materials

The compositions of the invention may contain an oil derived conditioning agent or mixture of oil derived conditioning agent. Suitable oil derived conditioning agents for use herein include water soluble vegetable and animal-derived emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives. One preferred class of oil derived conditioning agents for use herein having the general formula:



wherein n is from about 5 to about 200, preferably from about 20 to about 100, more preferably from about 30 to about 85, and wherein R comprises an aliphatic radical having on average from about 5 to 20 carbon atoms, preferably from about 7 to 18 carbon atoms.

25 Suitable ethoxylated oils and fats of this class include polyethyleneglycol derivatives of glyceryl cocoate, glyceryl caproate, glyceryl caprylate, glyceryl tallowate, glyceryl palmitate, glyceryl stearate, glyceryl laurate, glyceryl oleate, glyceryl ricinoleate, and glyceryl fatty esters derived from triglycerides, such as

palm oil, almond oil, and corn oil, preferably glyceryl tallowate and glyceryl cocoate.

Suitable oil derived conditioning agents of this class are available from Croda Inc. (New York, USA) under their Crovol (TN) line of materials such as
5 Crovol EP40 (PEG 20 evening primrose glyceride), Crovol EP 70 (PEG 60 evening primrose glyceride) Crovol A-40 (PEG 20 almond glyceride), Crovol A-70 (PEG 60 almond glyceride), Crovol M-40 (PEG 20 maize glyceride), Crovol M-70 (PEG 60 maize glyceride), Crovol PK-40 (PEG 12 palm kernel glyceride), and Crovol PK-70 (PEG 45 palm kernel glyceride) and under their Solan (TN) range
10 of materials such as Solan E, E50 and X polyethoxylated lanolins and Aqualose L-20 (TN) (PEG 24 lanolin alcohol) and Aqualose W15 (TN) (PEG 15 lanolin alcohol) available from Westbrook Lanolin. Further suitable surfactants of this class are commercially available from Sherex Chemical Co. (Dublin, Ohio, USA)
15 under their Varonic LI (TN) line of surfactants and from Rewo under their Rewoderm (TN) line of surfactants. These include, for example, Varonic LI 48 (polyethylene glycol (n=80) glyceryl tallowate, alternatively referred to as PEG 80 glyceryl tallowate), Varonic LI 2 (PEG 28 glyceryl tallowate), Varonic LI 420 (PEG 200 glyceryl tallowate), and Varonic LI 63 and 67 (PEG 30 and PEG 80 glyceryl cocoates), Rewoderm LI5-20 (PEG-200 palmitate), Rewoderm LIS-80 (PEG-200
20 palmitate with PEG-7 glyceryl cocoate) and Rewoderm LIS-75 (PEG-200 palmitate with PEG-7 glyceryl cocoate) and mixtures thereof. Other oil-derived emollients suitable for use are PEG derivatives of corn, avocado, and babassu oil, as well as Softigen 767 (TN) (PEG(6) caprylic/capric glycerides).

Also suitable for use herein are conditioning oils derived from composite
25 vegetable fats extracted from the fruit of the Shea Tree (*Butyrospermum Karkii Kotschy*) and derivatives thereof. This vegetable fat, known as Shea Butter is widely used in Central Africa for a variety of means such as soap making and as a barrier cream, it is marketed by Sederma (78610 Le Perray En Yvelines, France). Particularly suitable are ethoxylated derivatives of Shea butter available
30 from Karlshamn Chemical Co. (Columbus, Ohio, USA) under their Lipex (TN) range of chemicals, such as Lipex 102 E-75 and Lipex 102 E-3 (ethoxylated

mono, di-glycerides of Shea butter) and from Croda Inc. (New York, USA) under their Crovol (TN) line of materials such as Crovol SB-70 (ethoxylated mono, di-glycerides of Shea butter). Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used as conditioning agents in the compositions
5 according to the invention. Although these are classified as ethoxylated nonionic materials it is understood that a certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil derived hair and / or skin conditioning agents include ethoxylated derivatives of almond oil, peanut oil, rice bran oil, wheat germ oil,
10 linseed oil, jojoba oil, oil of apricot pits, walnuts, palm nuts, pistachio nuts, sesame seeds, rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil, pine oil, castor oil, soybean oil, avocado oil, safflower oil, coconut oil, hazelnut oil, olive oil, grapeseed oil, and sunflower seed oil.

Oil derived hair and /or skin conditioning agents highly preferred for use
15 herein include Lipex 102-3 (TN) (PEG-3 ethoxylated derivatives of Shea Butter) and Softigen 767 (TN) (PEG-6 caprylic/capric glycerides).

Surfactants

The compositions according to the present invention can further comprise one or more surfactants. Surfactants suitable for inclusion in compositions
20 according to the present invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms and can be selected from anionic, nonionic, amphoteric and cationic surfactants and mixtures thereof. The total level of surfactant is from about 1% to about 60%, preferably from about 2% to about 30%, more preferably from about 8% to about 25% and especially from about
25 10% to about 20% by weight.

The compositions herein may contain detergents surfactants, more preferably water-soluble detergents surfactants, although other surfactants may also be used. Especially preferred for use herein are surfactants selected from anionic, nonionic and amphoteric surfactants. Detergent surfactant, as defined
30 herein, means, any surfactant having a lipophilic chain length of from about 8

carbon atoms and greater and which is capable of providing hair and / or skin cleansing attributes. Water-soluble surfactants, as defined herein, means a surfactant which is capable of forming a clear isotropic solution when dissolved in water at 0.2 % w/w under ambient conditions (about 20°C).

5 The compositions of the invention preferably comprise a mixture of anionic and amphoteric surfactants with one or more nonionic surfactants. The level of the individual anionic components, where present, is preferably in the range of from about 0.1% to about 20%, more preferably from about 0.1% to about 15%, and especially from about 5% to about 15% by weight of the
10 composition, while the level of individual amphoteric or nonionic components, where present, is in the range from about 0.1% to about 15% by weight, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8% by weight.

Anionic surfactants suitable for inclusion in the compositions of the
15 invention include alkyl sulfates, ethoxylated alkyl sulfates, alkyl ethoxy carboxylates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycinate, N-acyl glutamates, acyl isethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their salts and/or their esters, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulfates,
20 acyl sarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain lengths for these surfactants are C₁₂-C₂₂, preferably C₁₂-C₁₈ more preferably C₁₂-C₁₄.

The compositions of the invention can comprise a total combined level of water-soluble anionic surfactant at a level of from about 0.1% to about 30%,
25 preferably from about 5% to about 20%, more preferably from about 10% to about 20% by weight.

Alkyl sulfate surfactants suitable for inclusion in the compositions of the present invention have the general formula (I):



30 wherein R is straight or branched chain alkyl or alkenyl, preferably straight chain alkyl, generally having a lipophilic chain length of from about 8 to about 22

carbon atoms and wherein M is selected from alkali metals, ammonium or other suitable monovalent cation or mixtures thereof. Suitable alkyl sulfates for use herein include lauryl sulfate (available from Albright and Wilson Ltd. under the trade name Empicol AL 30/T (TN)) and dodecyl alkyl sulfate.

5 Surfactants of this class include short-chain alkyl sulfate surfactants where 'short chain' as defined herein means a carbon chain length of about C₁₀ or less. Short chain alkyl sulfate surfactants are valuable in shampoo compositions for the delivery of good cleansing and product rinsing benefits in combination with a desirable lather profile and removal of cationic conditioning agents.

10 It should be understood that the definition of any particular carbon chain length, say C₁₀, may contain certain proportions of both higher and lower carbon chain lengths as a direct function of its synthesis. The level of such material can be controlled by modification of the process and the nature of the starting materials. Preferred for use herein are short chain alkyl sulfates wherein the
15 short chain length alkyl sulfate, in which at least about 50% w/w of the total alkyl sulphate content is C₁₀ or less, highly preferred for use herein are short chain alkyl sulfates wherein at least about 50% by weight of the total alkyl sulfate content is between about C₈ and about C₁₀, especially preferred for use herein are short chain alkyl sulphates wherein at least about 50% by weight of the total
20 alkyl sulfate content is C₁₀ alkyl sulfate. While C₁₀ alkyl sulfate is the preferred surfactant in the compositions of the invention, mixtures of short chain alkyl sulfates may also be used. Especially preferred in the shampoo compositions herein is short chain alkyl sulfate material containing at least about 80% by weight of the C₁₀, preferably at least about 90% C₁₀, more preferably at least
25 about 95% C₁₀ and especially at least about 97% C₁₀ alkyl sulfate. Suitable short chain alkyl sulfate materials are available from Albright and Wilson Ltd. under the trade name Empicol LC35 (TN). Preferably the level of short chain alkyl sulfate surfactant, where present, is at least about 0.5%, more preferably at least about 1% and most preferably at least about 2% by weight of the
30 composition.

Additional anionic surfactants suitable for use in the compositions according to the present invention are the salts of sulfuric acid esters of the reaction product of 1 mole of a higher fatty alcohol and from about 1 to about 12 moles of ethylene oxide, with sodium, ammonium and magnesium being the preferred counterions. Alkyl ethoxy sulfate surfactants are valuable in shampoo compositions for the delivery of good lather volume attributes in addition to hand mildness attributes. Suitable alkyl ethoxy sulfates have the general formula (II):



wherein R is straight or branched chain alkyl or alkenyl, preferably straight chain alkyl, generally having a lipophilic chain length of from about 8 to about 22 carbon atoms, x is the degree of ethoxylation and has an average value in the range of from about 2 to about 12, and wherein M is selected from alkali metals, ammonium or other suitable monovalent cation or mixtures thereof. The cation M should be chosen such that the salt of the anionic surfactant is water-soluble.

Solubility will depend upon the particular mixture of anionic surfactant and cations chosen.

Preferred for use herein are the alkyl ethoxy sulfates containing an average degree of ethoxylation (x) of from about 2 to 6, preferably 2 to 4 moles of ethylene oxide, such as ammonium laureth-2 sulfate, ammonium laureth-3 sulfate and sodium laureth-3 sulfate. In preferred embodiments, the anionic surfactant contains at least about 50% especially at least about 75% by weight of ethoxylated alkyl sulfate.

In addition to the broad range ethoxylated alkyl sulfates obtained via conventional sodium catalysed ethoxylation techniques and subsequent sulphation processes, ethoxylated alkyl sulfates obtained from narrow range ethoxylates (NREs) are also suitable water-soluble anionic surfactants for use in the present compositions. Preferred narrow range ethoxylated alkyl sulfates suitable for use herein are selected from sulfated alkyl ethoxylates containing on average from about 1 to about 6, preferably from about 2 to about 6, more preferably from about 3 to about 4 and especially about 3 moles of ethylene oxide, such as, NRE sodium laureth-3 sulfate. NRE materials suitable for use

herein contain distributions of the desired ethylene oxide (EO_n) in combination with both higher ethoxylates (EO_{n+1}), (EO_{n+2}), (EO_{n+3}) and so on, and lower ethoxylates, (EO_{n-1}), (EO_{n-2}), (EO_{n-3}) and so on. Preferred NRE materials for use herein contain an ethoxylate distribution such that the total amount of EO_n ,

5 EO_{n+1} and EO_{n-1} is greater than the total amount of the other ethoxylates (calculated on a weight percent basis). NRE materials highly preferred for use herein contain distributions of the desired ethylene oxide (EO_n) in the ranges of from 15% to about 45% by weight of EO_n , from about 10% to about 25% by weight of EO_{n+1} and from about 10% to about 25% by weight of EO_{n-1} . Highly

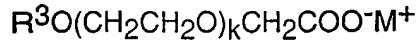
10 preferred NRE materials contain less than about 9% by weight of ethoxylated alkyl sulfate having 7 or more moles of ethylene oxide and less than about 13% by weight of non-ethoxylated alkyl sulfate. Suitable laureth 3 sulfate NRE materials are available from Hoechst under the trade names GENAPOL ZRO (TN) Narrow Range and GENAPOL (TN) Narrow Range.

15 Preferred for use herein is a mixture of alkyl sulfate and alkyl ethoxy sulfate anionic surfactants at a total level of from about 0.1% to about 30%, preferably from about 5% to about 20%, especially from about 10% to about 20% by weight. The individual level of each of the separate anionic components is in the range from about 0.1% to about 20%, preferably from about 0.1% to

20 about 15%, and especially from about 5% to about 15% by weight of the composition. Especially preferred for use herein is a mixture of lauryl sulfate (available from Albright and Wilson Ltd. under the trade name Empicol AL 30/T (TN)) and C₁₂/14AE₃S (available from Albright and Wilson Ltd. under the trade names Empicol AEB/T, AEC/T and AEC 70 (TN)) wherein the ratio of alkyl sulfate to alkyl ethoxy sulfate is in the range of from about 5:1 to about 1:5, preferably from about 3:1 to about 1:3, more preferably from about 1:1 to about 1:3.

30 The compositions of the present invention may contain alkyl ethoxy carboxylate surfactant. Alkyl ethoxy carboxylate surfactant is valuable in compositions for the delivery of good rinsing performance and desirable lather characteristics.

Alkyl ethoxy carboxylates have the general formula (III):



wherein R³ is a C₁₀ to C₁₅ alkyl or alkenyl group, preferably a C₁₁-C₁₅, more preferably a C₁₂-C₁₄ alkyl or C₁₂-C₁₃ alkyl group, k is an average value of ethoxylation ranging from 2 to about 7, preferably from about 3 to about 6, more preferably from about 3.5 to about 5.5, especially from about 4 to about 5, most preferably from about 4 to about 4.5, and M is a water-solubilizing cation, preferably an alkali metal, alkaline earth metal, ammonium, lower alkanol ammonium, and mono-, di-, and tri-ethanol ammonium, more preferably sodium, potassium and ammonium, most preferably sodium and ammonium and mixtures thereof with magnesium and calcium ions.

Water-soluble anionic alkyl ethoxy carboxylate surfactants suitable for use herein are the C₁₂ to C₁₄ (average EO 3-6) ethoxy carboxylates and the C₁₂ to C₁₃ (average EO 3-6) ethoxy carboxylates. Suitable materials include salts of NEODOX 23-4 (TN) available from Shell Inc. (Houston, Texas, USA). Preferred for use herein are alkyl ethoxy carboxylate surfactants wherein, when R³ is a C₁₂-C₁₄ or C₁₂-C₁₃ alkyl group and the average value of k is in the range of from about 3 to about 6, more preferably from about 3.5 to about 5.5, especially from about 4 to about 5 and most preferably from about 4 to about 4.5.

The compositions of the present invention may also comprise water-soluble nonionic surfactants. Exemplary nonionic surfactants are selected from ethoxylated alcohols, C₁₂-C₁₄ fatty acid mono-and dialkanolamides such as cocoethanolamide, cocomonoisopropylamide and ethoxylated derivatives thereof, alkyl polysaccharides such as C₁₀-C₁₈ alkyl polyglycosides and polyhydroxy fatty acid amide surfactants.

The nonionic surfactant is preferably used in combination with other surfactants such as anionic and / or amphoteric. Nonionic surfactant is generally used at levels of from about 0.1% to about 15%, preferably from about 0.1% to about 10%, more preferably from about 0.1% to about 8%, most preferably from about 0.5% to about 5% and especially from about 0.5% to about 2% by weight in the compositions of the present invention.

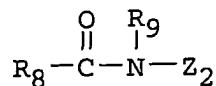
Ethoxylated alcohol surfactants suitable for use herein include monohydric, dihydric and polyhydric alcohol mono- and poly- ethoxylates and / or alkylated derivatives thereof. Preferred for use herein are ethoxylated alcohol surfactants having the general formula (IV):



wherein R_1 is C₄-C₃₁ hydrocarbyl, preferably C₆-C₁₉ hydrocarbyl, more preferably C₉-C₁₁ hydrocarbyl, most preferably C₇-C₁₁ hydrocarbyl, including natural or synthetic materials having straight-chain, branched chain alkyl and / or alkenyl configuration, R_2 is typically, hydrogen, C₁-C₈ alkyl or hydroxyalkyl and x is an average value of ethoxylation ranging from 1 to about 20, preferably from about 5 to about 15, more preferably from about 5 to about 12, most preferably from about 7 to about 10. Other ethoxylates corresponding to the formula, such as those formed from one or more alcohols such as butanol, isobutanol, hexanol, octanol, decanol, dodecanol, tetradecanol, pentadecanol, octadecanol, eicosanol, docosanol, tetracosanol and triacontanol, are also suitable for use herein.

Exemplary alcohol ethoxylates for use herein are those wherein R_2 is hydrogen. Preferred for use herein are C₉ to C₁₁ alcohols having an average degree of ethoxylation of about 6 (available from Shell under the trade name Dobanol 91-6 (TN)) and C₉ to C₁₁ alcohols having an average degree of ethoxylation of about 8 (available from Shell under the trade name Dobanol 91-8 (TN)).

Polyhydroxy fatty acid amide surfactants suitable for use herein include those having the general formula (V).



The preferred N-alkyl, N-alkoxy or N-aryloxy, polyhydroxy fatty acid amide surfactants according to formula (V) are those in which R_8 is C₅-C₃₁ hydrocarbyl, preferably C₆-C₁₉ hydrocarbyl, including straight-chain and branched chain alkyl and alkenyl, or mixtures thereof and R_9 is typically, hydrogen, C₁-C₈ alkyl or hydroxyalkyl, preferably methyl, or a group of formula -

R^1-O-R^2 wherein R^1 is C_2-C_8 hydrocarbyl including straight-chain, branched-chain and cyclic (including aryl), and is preferably C_2-C_4 alkylene, R^2 is C_1-C_8 straight-chain, branched-chain and cyclic hydrocarbyl including aryl and oxyhydrocarbyl, and is preferably C_1-C_4 alkyl, especially methyl, or phenyl. Z_2 is

5 a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyLATED derivative (preferably ethoxylated or propoxylated) thereof. Z_2 preferably will be derived from a reducing sugar in a reductive ammoniation reaction, most preferably Z_2 is

10 a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z_2 . It should be

15 understood that it is by no means intended to exclude other suitable raw materials. Z_2 preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH_2OH$, $-CH(CH_2OH)-(CHOH)_{n-1}-CH_2H$, $CH_2(CHOH)_2(CHOR')CHOH-CH_2OH$, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly-saccharide, and alkoxyLATED

20 derivatives thereof. As noted, most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

The most preferred polyhydroxy fatty acid amide has the formula $R_8(CO)N(CH_3)CH_2(CHOH)_4CH_2OH$ wherein R_8 is a C_6-C_{19} straight chain alkyl or alkenyl group. In compounds of the above formula, $R_8-CO-N<$ can be, for

25 example, cocoamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmamide, tallowamide, etc.

A preferred process for making the above compounds having formula (V) comprises reacting a fatty acid triglyceride with an N-substituted polyhydroxy amine in the substantial absence of lower (C_1-C_4) alcoholic solvent, but

30 preferably with an alkoxyLATED alcohol or alkoxyLATED alkyl phenol such as NEODOL and using an alkoxide catalyst at temperatures of from about 50°C to

about 140°C to provide high yields (90-98%) of the desired products. Suitable processes for making the desired polyhydroxy fatty acid amide compounds are outlined in US-A-5,194,639 and US-A-5,380,891.

It should be recognised that along with the polyhydroxy fatty acid amides, 5 the processes used to form them can also typically produce quantities of nonvolatile by products such as esteramides and cyclic polyhydroxy fatty acid amide. The level of these by-products will vary depending upon the particular reactants and process conditions. The suitable processes referred to above are advantageous in that they can yield rather low levels of by-products, including 10 such cyclic amide by-product.

The polyhydroxy fatty acid amide surfactants suitable for use herein offer the additional advantages to the formulator that they can be prepared wholly or primarily from natural, renewable, non petrochemical feed stocks and are degradable. They also exhibit low toxicity to aquatic life.

15 Additional nonionic surfactants suitable for use herein include: long chain tertiary amine oxides corresponding to the following general formula:



wherein R_1 contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, 20 and from 0 to about 1 glyceryl moiety, and R_2 and R_3 contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals. the arrow in the formula is a conventional representation of a semipolar bond; Long chain tertiary phosphine oxides corresponding to the following general formula:



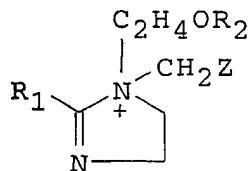
wherein R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety and R' and R'' are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms. Long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from about 1 to about 3 carbon atoms (usually methyl) 30

and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety.

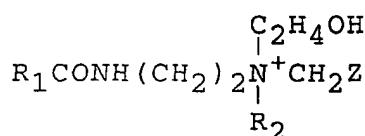
The compositions for use herein may also contain a water-soluble 5 amphoteric surfactant at a level of from about 0.1% to about 15% by weight, preferably from about 0.5% to about 10%, more preferably from about 1% to about 8%, most preferably from about 1% to about 5% by weight.

Amphoteric surfactants suitable for use herein include zwitterionics such as betaines, amido betaines and sultaines as well as:

10 (a) imidazolinium surfactants of formula (VI)



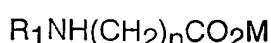
wherein R₁ is C₇-C₂₂ alkyl or alkenyl, R₂ is hydrogen or CH₂Z, each Z is independently CO₂M or CH₂CO₂M, and M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium; and/or ammonium derivatives of 15 formula (VII)



wherein R₁, R₂ and Z are as defined above;

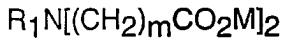
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(b) aminoalkanoates of formula (VIII)

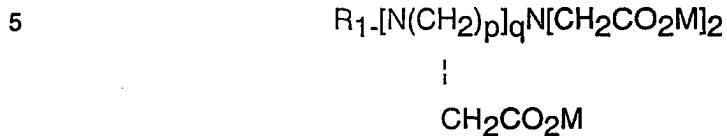


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iminodialkanoates of formula (IX)



and iminopolyalkanoates of formula (X)



wherein n, m, p, and q are numbers from 1 to 4, and R₁ and M are
10 independently selected from the groups specified above; and

(c) mixtures thereof.

Suitable amphoteric surfactants of type (a) are marketed under the trade
15 name Miranol and Empigen and are understood to comprise a complex mixture
of species. Traditionally, the Miranols have been described as having the
general formula VI, although the CTFA Cosmetic Ingredient Dictionary, 3rd
Edition indicates the non-cyclic structure V while the 4th Edition indicates yet
another structural isomer in which R₂ is O-linked rather than N-linked. In
20 practice, a complex mixture of cyclic and non-cyclic species is likely to exist and
both definitions are given here for sake of completeness. Preferred for use
herein, however, are the non-cyclic species.

Examples of suitable amphoteric surfactants of type (a) include
compounds of formula VI and/or VII in which R₁ is C₈H₁₇ (especially iso-capryl),
25 C₉H₁₉ and C₁₁H₂₃ alkyl. Especially preferred are the compounds in which R₁
is C₉H₁₉, Z is CO₂M and R₂ is H; the compounds in which R₁ is C₁₁H₂₃, Z is
CO₂M and R₂ is CH₂CO₂M; and the compounds in which R₁ is C₁₁H₂₃, Z is
CO₂M and R₂ is H.

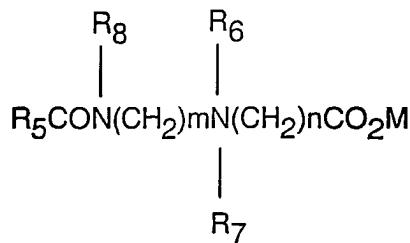
In CTFA nomenclature, materials suitable for use in the present invention
30 include cocoamphocarboxypropionate, cocoamphocarboxy propionic acid, and
especially cocoamphoacetate and cocoamphodiacetate (otherwise referred to as

cocoamphocarboxyglycinate). Specific commercial products include those sold under the trade names of Ampholak 7TX (TN)(sodium carboxy methyl tallow polypropyl amine), Empigen CDL60 (TN) and CDR 60 (TN) (Albright & Wilson), Miranol H2M Conc. (TN), Miranol C2M Conc. N.P.(TN), Miranol C2M Conc. 5 O.P.(TN), Miranol C2M SF (TN), Miranol CM Special (TN) (Rhône-Poulenc); Alkateric 2CIB (TN) (Alkaril Chemicals); Amphoterge W-2 (TN)(Lonza, Inc.); Monateric CDX-38 (TN), Monateric CSH-32 (TN) (Mona Industries); Rewoteric AM-2C (TN) (Rewo Chemical Group); and Schercotic MS-2 (TN) (Scher Chemicals).

10 It will be understood that a number of commercially-available amphoteric surfactants of this type are manufactured and sold in the form of electroneutral complexes with, for example, hydroxide counterions or with anionic sulfate or sulfonate surfactants, especially those of the sulfated C₈-C₁₈ alcohol, C₈-C₁₈ ethoxylated alcohol or C₈-C₁₈ acyl glyceride types. Preferred from the viewpoint 15 of mildness and product stability, however, are compositions which are essentially free of (non-ethoxylated) sulfated alcohol surfactants. Note also that the concentrations and weight ratios of the amphoteric surfactants are based herein on the uncomplexed forms of the surfactants, any anionic surfactant counterions being considered as part of the overall anionic surfactant component 20 content.

Examples of preferred amphoteric surfactants of type (b) include N-alkyl polytrimethylene poly-, carboxymethylamines sold under the trade names Ampholak X07 (TN) and Ampholak 7CX (TN) by Berol Nobel and also salts, especially the triethanolammonium salts and salts of N-lauryl-beta-amino 25 propionic acid and N-lauryl-imino-dipropionic acid. Such materials are sold under the trade name Deriphat (TN) by Henkel and Miritaine (TN) by Rhône-Poulenc.

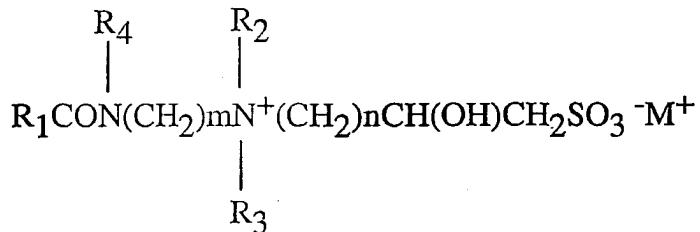
Betaine surfactants suitable for use herein include alkyl betaines of the formula R₅R₆R₇N⁺ (CH₂)_nCO₂M and amido betaines of the formula (XI):



wherein R₅ is C₁₁-C₂₂ alkyl or alkenyl, R₆ and R₇ are independently C₁-C₃ alkyl, R₈ is hydrogen or methyl, M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium, and n, m are each numbers from 1 to 4.

5 Preferred betaines include cocoamidopropyl dimethylcarboxymethyl betaine and laurylamidopropyl dimethyl carboxymethyl betaine.

Water-soluble sultaine surfactants suitable for inclusion in the compositions of the present invention include alkylamido sulfonates of the formula:

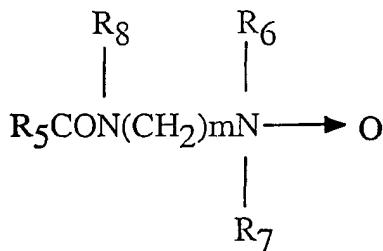


10

wherein R₁ is C₇ to C₂₂ alkyl or alkenyl, R₂ and R₃ are independently C₁ to C₃ alkyl, R₄ is hydrogen or methyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m and n are numbers from 1 to 4. Preferred for use herein is coco amido propylhydroxy sultaine.

15

Water-soluble amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide R₅R₆R₇NO and amido amine oxides of the formula:



wherein R₅ is C₁₁ to C₂₂ alkyl or alkenyl, R₆ and R₇ are independently C₁ to C₃ alkyl, R₈ is hydrogen or methyl, M is H, alkali metal, alkaline earth metal, ammonium or alkanolammonium and m is a number from 1 to 4.

5 Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

Cationic surfactants suitable for use herein include quaternary ammonium surfactants selected from mono C₈ - C₁₆, preferably C₁₀ - C₁₄ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted 10 by methyl hydroxy ethyl or hydroxy propyl groups. Exemplary cationic surfactants for use herein include: di hydrogenated tallowamidoethyl hydroxyethylammonium methosulfate, available under the trade name Varisoft CB110 (TN) from Witco. It should be understood that cationic quaternary ammonium surfactants can act as conditioning cosmetic agents in the 15 compositions herein.

Surfactants commonly used in hair dye compositions include trideceth-2 carboxamide MEA, ceteareth-30, PEG2-Oleamine, Oleth-30, MEA laureth sulfate, deceth-3, deceth-5, laureth-15, laureth-12, lauric acid, C12-C15 pareth-3, oleamide MIPA, C11-C15 pareth-9, polysorbate-20, nonyl nonosynol 49, 20 lauramide DEA, soytrimonium chloride, oleth 10, oleth 2, dicetyldiammonium chloride, hydroxyethylcetyltrimmonium phosphate, dilinoeic acid, linoleamidopropyldimethylaminodimer dilinoleate.

Solvents

Suitable solvents include, but are not limited to, water, butoxydiglycol, 25 propylene glycol, alcohol (denat.), ethoxydiglycol, isopropylalcohol, hexylene glycol, benzyl alcohol.

EXPERIMENTALS

All results discussed herein were obtained by testing chelants according to the following protocols. The chelants tested can be obtained from any usual supplier.

5 **Hydrogen Peroxide Decomposition Ratio Measurement Protocol**

The Hydrogen Peroxide Decomposition Ratio Measurement Protocol is defined as follows: 6.0% by weight of concentrated ammonium hydroxide (30% active ammonia) is added to deionised water and the pH of the solution is adjusted to 10 using acetic acid. 300ppm of copper sulphate and 0.026M of the 10 chelant to be tested are added to said composition. 10ml of this solution is then mixed with 1ml of hydrogen peroxide (35% active). The initial level of hydrogen peroxide is measured at this moment ($t=0$); the final level of hydrogen peroxide is measured after 30 minutes. The value of the ratio of the hydrogen peroxide concentration at $t=0$ and at $t=30\text{mn}$ is the Hydrogen Peroxide Decomposition 15 Ratio (% Loss).

The initial and final level of hydrogen peroxide can be measured according to any standard technique. The following is a well-known and standard technique that was used by the inventors: 0.2 - 0.3g (the exact quantity being precisely measured) of the solution to be titrated is added to 40ml of 10% acetic 20 acid. The autotitrator (Mettler DL58 Autotitrator) adds 20ml of potassium iodide solution (15% in water), 5ml of ammonium molybdate solution (2% in water) and titrates (while stirring) with 0.1M sodium thiosulphate solution. The level of hydrogen peroxide (% Peroxide) is then calculated from the following equation:

$$\% \text{Peroxide} = \frac{\text{end-point (in ml)} \times \text{molarity of sodium thiosulphate} \times 34.02}{2 \times 10 \times \text{sample weight (in g)}}$$

25 34.02 being the molecular weight of Hydrogen Peroxide.

Three replicate runs are made at both $t = 0$ and $t = 30\text{mn}$ and then averaged to calculate the Hydrogen Peroxide Decomposition Ratio (% Loss).

Chelants having a Hydrogen Peroxide Decomposition Ratio (% Loss) of less than 10% are preferred for use herein. Preferably the value of the Hydrogen

Peroxide Decomposition Ratio is less than 3.5%, more preferably less than 3%, even more preferably less than 2.0%.

Oxidative Hair Treatment Protocol

For each chelant tested, seven switches of virgin dark hair were used.

5 "Virgin hair" means hair that has never been treated chemically and can be bought, for example, at Hugo Royer International Ltd, 10 Lakeside Business Park, Swan Park, Sandhurst, Berkshire, GU47 9ND. The switches usually weighed about 1.5g each and are treated stepwise according to the following protocol.

10 A bleaching composition comprising the chelant to be tested is prepared by mixing in equal weight amounts a hydrogen peroxide emulsion base and an alkaline (high pH) emulsion base.

The hydrogen peroxide emulsion base contains:

- 15 a) 35% by weight of an emulsion base premix comprising 10 % stearyl alcohol and 5% cetereth25;
- b) 25% of an stabilizing solution comprising 1% tetrasodium DTPA, 0.4% HEDP, 1% sodium hydroxide (32% purity) and water q.s.p
- c) 14% of water;
- d) 26% of a solution of hydrogen peroxide (35% purity).

20 The alkaline emulsion base contains:

- a) 0.2% by weight of sodium sulphite;
- b) 0.2% of ascorbic acid;
- c) 3% of ammonium acetate;
- d) 44.5% of the same emulsion base premix used for the hydrogen peroxide emulsion base;
- e) 11% of an ammonia solution (30% purity) to set the pH to approximately 10;
- f) the amount to be tested of chelant or mixtures of chelants (for example 3.8% by weight of the alkaline emulsion base of EDDS, equivalent to 1.9% EDDS "on head");

g) q.s. of water.

The pH of the mixture is buffered to 10 by the alkaline emulsion base.

2g of the bleaching composition per g of hair to be treated was applied on the hair switches and massaged in thoroughly. The hair switches were then 5 wrapped in a plastic film and put in an oven at 30°C. After 30mn, they were removed from the oven and from the wrapping film and rinsed for 1mn in water. 0.1g of shampoo per g. of hair was then added and milked for 30s at a rate of at least 150 strokes a minute before rinsing for 30s. The combined concentration of calcium and magnesium ions (water hardness) of the water used during all 10 experiments (except for the preparation of the compositions tested, wherein water was distilled or dionised) was carefully kept at 9 grains per gallon (153 ppm), with a molar ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ equal to 3:1. The concentration of copper (Cu^{2+}) ions was kept at about 1 ppm (+/- 10%), the exact concentrations being measured by a standard analytic method. The rinsing water flow was adjusted to 15 6 liters per minute). The same shampooing and rinsing process was repeated another time (this is the "Oxidative Hair Treatment Protocol With 2 Intermediate Washes" referred to in the claims) or 9 additional times (this is the "Oxidative Hair Treatment Protocol With 10 Intermediate Washes" referred to in the claims) depending on the Damage Assessment Protocol used. The excess water was 20 then squeezed out of the hair, and the hair dried with a fan. Any standard shampoo can be used in this protocol as long as it is free from transition metal ions such as copper ion and that the level chelants is less than 0.1% by weight of the shampoo. Prell® shampoo was using during these tests.

This Oxidative Hair Treatment Protocol can be repeated several times. 25 When damage is measured according to the FT-IR Damage Assessing Protocol or to the Goniophotometer Damage Assessing Protocol (both described below) the Oxidative Hair Treatment Protocol is preferably repeated 5 times. This process is described as a 5-Cycle Oxidative Hair Treatment Protocol With 2 or 10 Intermediate Washes.

Two different test methods were used to assess the protection conferred to hair by the compositions according to the present invention. These methods (FT-IR and Goniophotometer Damage Assessing Protocol) are described in details below.

5 **FT-IR Damage Assessing Protocol**

Damage caused to the hair was assessed by the FT-IR (Fourier Transform Infrared) method, which has been established to be suitable for studying the effects of oxidative treatments on hair (Strassburger, J., *J. Soc. Cosmet. Chem.*, 36, 61-74 (1985); Joy, M. & Lewis, D.M., *Int. J. Cosmet. Sci.*, 10, 13, 249-261 (1991); Signori, V. & Lewis, D.M., *Int. J. Cosmet. Sci.*, 19, 1-13 (1997)). In particular, these authors have shown that the method is suitable for quantifying the amount of cysteic acid that is produced from the oxidation of cystine. In general, the oxidation of cystine is thought to be a suitable marker by which to monitor the overall oxidation of the keratinous part of the fiber.

15 Net, the measurement of cysteic acid units by FT-IR is commonly used to study the effects of oxidative treatments or environmental oxidation upon keratin protein containing fibers such as hair and wool.

Signori & Lewis (D.M., *Int. J. Cosmet. Sci.*, 19, 1-13 (1997)) have shown that FT-IR using a diamond Attenuated Total Internal Reflection (ATR) cell is a sensitive and reproducible way of measuring the cysteic acid content of single fibers and bundles. They have shown that this technique is more suitable than using the FT-IR method in simple transmission or microscope modes. They have also shown that the diamond cell ATR was significantly more sensitive and reproducible than the ZnSE cell. Hence, the method that we have employed to 20 measure the cysteic acid content of multiple fiber bundles and full hair switches, is based upon the FTIR diamond cell ATR method employed by Signori and Lewis (1997). The detailed description of the method used for testing the different damage inhibitors follows thereafter:

25 A Perkin Elmer Spectrum® 1 Fourier Transform Infrared (FTIR) system equipped with a diamond Attenuated Total Internal Reflection (ATR) cell was 30

used to measure the cysteic acid concentration in human hair. In this method, hair switches of various sizes and colours can be used. The switches were platted (~1 plait per cm) in order to minimize variations in surface area of contact between readings. The Oxidative Hair Treatment Protocol described above was 5 repeated for 5 cycles to mimic the behavior of hair after repeated bleaching cycles. Following this treatment, four readings per switch were taken (~1/3 and 2/3s down the switch on both sides), and an average calculated. Backgrounds were collected every 4 readings, and an ATR cell pressure of 1N/m was employed. The cell was cleaned with ethanol between each reading, and a 10 contamination check performed using the monitor ratio mode of the instrument. As prescribed by Signori & Lewis in 1997, a normalized double derivative analysis routine was used. The original spectra were initially converted to absorbance, before being normalized to the 1450cm⁻¹ band (the characteristic and invariant protein CH₂ stretch). This normalized absorbance was then twice 15 derivatised using a 13 point averaging. The value of the 1450cm⁻¹ normalized 2nd derivative of the absorbance at 1040cm⁻¹ was taken as the relative concentration of cysteic acid. This figure was multiplied by -1x10⁻⁴ to recast it into suitable units. It was found that virgin human hair produced a value of ~20 cysteic acid 20 units, and heavily oxidized hair produced values of >170. The following instrumental conditions were employed:

Spectral Resolution -	4cm ⁻¹
Data Interval -	0.7cm ⁻¹
Mirror Scan Speed -	0.2cms ⁻¹
Number of Background Scans -	20
25 Number of Sample Scans -	20
Scan Range -	4000cm ⁻¹ to 600cm ⁻¹

Using these instrumental conditions and the 2nd derivative analysis routine, it was found that the sensitivity and reproducibility of the method in the range 10 to 150 cysteic acid units, are both ~±5-10%.

30 Goniophotometer Damage Assessing Protocol

Damage caused to the hair was also assessed by the Goniophotometer method, which has been established to be suitable for studying the effects of changes in surface condition of the hair (R. F. Stamm, M. L. Garcia and J. J. Fuchs, 'The Optical Properties of Human Hair-I. Fundamental Consideration and 5 Goniophotometer Curves', and 'II. The Lustre of Human Hair Fibres', J Soc. Cosmet. Chem. 28, 571-599 and 601-609 (September 1977)). It has been demonstrated that the shine (gloss or lustre) is proportional to the relative amounts of specularly and diffusely reflected light (I_s and I_d respectively). This is dictated by the refractive index of the fibre and the roughness of the surface. By 10 coating the hair fibres in a very fine coating of gold before measuring the reflected light the internal reflection of the fibre is eliminated and the shine can be used as a sensitive measure of the roughness of the surface. For example, a smooth surface will reflect light that has a large specular content and a small diffuse content

15 A GP200 Goniophotometer was used from Murakami Colour Research Laboratory. The gold coating was applied using an Emitech K-500 sputter coater.

Randomly chosen single fibres were loaded onto a single fibre holder (10 fibres per holder) and held in a parallel array. A minimum of 12 holders were 20 loaded giving good reproducibility of +/- 4%. Each single fibre holder was coated in gold using the Emitech sputter coater for 1 minute with a 25mA coating rate. This gives a coating of between 10-300nm of gold on the surface. The sample holder was then loaded into the GP200 Goniophotometer. The following instrumental conditions were employed:

25 Reflection measurement mode – fixed incident angle, variable receiving angle

Incidence Angle = +30

Detector Angle range = -30 to +60

Light aperture values: Incident = 4.0; Receiving = 2.0

30 Inclination of specimen table = 0 deg

Sensitivity = 850

High voltage of photomultiplier = 725

For each set of fibres a reflectance spectrum is obtained. From this spectrum the reflectance peak maximum (I_{max}) is normalised to 1 and all the other reflectances are scaled according to this maximum

5

$$I(\text{norm}) = I/I_{max}$$

Where $I(\text{norm})$ = normalised intensity, I = reflectance intensity, I_{max} = reflectance peak maximum.

10 The shine is calculated from the difference between the specular reflection and diffuse reflection at 0° divided by the width of the specular peak at its half maximum (in angular units)

$$S(\text{norm}) = [(1 - I(0)) / \sigma] * 100$$

15 Where $S(\text{norm})$ = normalised shine, $I(0)$ = normalised reflectance at 0° , σ = angular full width at half maximum in $^\circ$.

COMPARATIVE TESTS

Damages measured according to the FTIR-IR Damage Assessing Protocol

The following illustrates the effect of EDDS and 4 other chelants:
 20 ethylenediaminetetraacetic acid (EDTA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP), diethylenetriaminepentaacetate (DTPA) and diethylenetriamine-N,N,N',N'',N''-penta(methylene phosphonate) (DTPMP). The weight percentages for each chelant are indicated in the first line of the table below. The tri-sodium salt of EDDS, tetra-sodium salt of EDTA, di-sodium salt of HEDP, penta-sodium
 25 salt of DTPA and tetra-sodium salt of DTPMP were used.

In this experiment EDDS was tested at 1.9% by weight on head, but EDDS also provides excellent benefits at much lower concentrations. Damage and lightening effects were assessed after 5 cycles according to the Oxidative Hair Treatment Protocol With 2 Intermediates Washes as described above.
 30 Human hair is often bleached or dyed 5 times or more during its life, which

makes this 5 cycle test very meaningful. The results are shown in the table below:

Weight % ("on-head")	1.9% EDDS	2.0% EDTA	2.0% HEDP	2.65% DTPA	3.8 % DTPMP
Damage after 5 cycles (cysteic acid units)	110	165	163	147	142
Damage benefit vs EDTA 2%	+ 33 %	-	+ 1 %	+ 11 %	+14 %

Hair treated with 1.9% by weight EDDS displayed much less damage than hair treated with any other chelant. However increasing the level of any chelants allows reducing oxidative damage to value below 160 cysteic acid units. The value for damage without any added chelant is about 170 damaged cysteic units. The lightening effect of the oxidative composition was of about the same quality for all compositions.

Damages measured by the Goniophotometer Damage Assessing Protocol

The following illustrates the effect of EDDS, HPPDS and 4 others chelants: EDTA, HEDP, DTPA and DTPMP. The tri-sodium salt of EDDS, tetra-sodium salt of HPPDS, tetra-sodium salt of EDTA, di-sodium salt of HEDP, penta-sodium salt of DTPA and tetra-sodium salt of DTPMP were used. The corresponding weight percentage is indicated in the first line of the table below.

Damage was assessed after 5 cycles according to the Oxidative Hair Treatment Protocol With 10 Intermediate Washes described above (at least 11 measures for each chelant were made and averaged to give the values compiled below).

The normalized shine can slightly vary depending on the type of virgin hair used as starting material. In order to obtain data that are independent of the starting material, the normalized shine values obtained as described above have been subsequently divided by the value obtained for virgin (untreated) hair.

Weight %	0.95% EDDS	0.97% HPPDS	1.0% EDTA	1.0% HEDP	1.32% DTPA	1.90% DTPMP
Normalized shine ratio (hair treated after 9 cycles / virgin hair)	1.03	1.00	0.704	0.730	0.757	0.92

EXAMPLES

The following examples illustrate oxidative dye compositions according to the present invention and methods of manufacture thereof. It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

Examples of formulation: emulsion

	1	2	3	4	5	6	7	8	9	10
Sodium sulphite	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ascorbic Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ammonium Acetate	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Ammonia (30% active)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Ceteareth 25	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Stearyl Alcohol	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Sodium Benzoate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Phenoxyethanol	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
DTPMP (tetrasodium salt of)	2.5	-	2.5	-	-	1.0	-	1.0	0.5	3.0
DTPA (pentasodium salt of)	-	-	0.5	1.0	-	-	0.5	-	0.5	-
EDDS (trisodium salt of)	-	1.0	-	1.0	0.5	1.0	1.0	1.0	0.5	-
Para-phenylene diamine	0.8	0.5	0.6	0.5	0.8	0.8	0.5	0.6	0.5	0.8

Para-aminophenol	0.2	0.3	0.2	0.1	0.2	0.2	0.3	0.2	0.1	0.2
Meta-aminophenol	1.0	0.5	1.0	0.6	1.0	1.0	0.5	1.0	0.6	1.0
Resorcinol	1.6	1.2	1.6	0.8	1.6	1.6	1.2	1.6	0.8	1.6
Hydrogen Peroxide (35% active)	8.6	8.6	8.6	12.9	17	17	17	34	34	34
Trimethylsilylamo- dimethicone (SF1708)	0.5	0.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Polyquaternium 10 (Polymer JR30M)	0.2	0.2	-	0.2	0.2	0.2	0.2	-	-	-
Xanthan gum	0.5	0.5	-	1.0	0.5	0.5	0.5	0.5	0.5	1.0
Cetyl hydroxyethyl Cellulose (Natrosol 330CS Plus)	-	-	0.8	1.0	0.8	0.5	0.5	0.5	0.5	1.0
pH adjust to pH 10	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs
Water	qs	qs	qs	qs	qs	qs	qs	qs	qs	qs

Examples of formulation: thickened aqueous solution

	1	2	3	4	5	6	7	8	9	10
Sodium sulphite	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ascorbic Acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Citric Acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ammonia (30% active)	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Acrylates Copolymer (Aculyn® 33A)	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Oleth 10	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Oleth 2	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Oleic Acid	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Cocamide DEA	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0

DTPMP (tetrasodium salt of)	2.5	-	2.5	-	-	1.0	-	1.0	0.5	3.0
DEPTA (pentasodium salt of)	-	-	0.5	1.0	-	-	0.5	-	0.5	-
EDDS (trisodium salt of)	-	1.0	-	1.0	0.5	1.0	1.0	1.0	0.5	-
Para-phenylene diamine	0.8	0.5	0.6	0.5	0.8	0.8	0.5	0.6	0.5	0.8
Para-aminophenol	0.2	0.3	0.2	0.1	0.2	0.2	0.3	0.2	0.1	0.2
Meta-aminophenol	1.0	0.5	1.0	0.6	1.0	1.0	0.5	1.0	0.6	1.0
Resorcinol	1.6	1.2	1.6	0.8	1.6	1.6	1.2	1.6	0.8	1.6
Hydrogen Peroxide (35% active)	8.6	8.6	8.6	13	17	17	17	34	34	34
Behentrimonium Chloride	0.5	0.5	1.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Dicetyltrimonium Chloride	0.2	0.2	0.7	0.2	0.2	0.2	0.2	-	-	-
Acrylates Steareth-20	0.5	0.5	-	1.0	0.5	0.5	0.5	0.5	0.5	1.0
Methacrylate Copolymer (Aculyn ® 22)										
Propylene Glycol	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2
Ethoxy Diglycol	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2
pH adjust to pH 10	qs									
Water	qs									

The above compositions are useful for dyeing hair with reduced damage.

Similar compositions not including oxidative dye precursors and couplers (in the above examples para-aminophenol, meta-aminophenol and resorcinol) can be
5 used for bleaching (lightening) hair.

Oxidative hair dye compositions are usually sold in kits comprising, in separate containers, a dye component (also called "dye cream" for emulsion or "dye liquid" for solution) comprising the oxidative dye precursors (and usually the Hair Swelling Agent) and a hydrogen peroxide component (also called "hydrogen peroxide cream" for emulsion or "hydrogen peroxide liquid" for solution)
10

comprising the oxidizing agent (usually hydrogen peroxide). The consumer mixes the dye component and hydrogen peroxide component immediately before use. The examples of the tables above illustrate the resulting mixtures.

Similarly, bleaching compositions are usually sold as a kit comprising two 5 or three separate containers. The first contains the hair-swelling agent (e.g. ammonia), the second contains the oxidizing agent and the third (optional) contains a second oxidizing agent (e.g. alkali or ammonium salt of persulphates, percarbonate, perborate). The bleaching compositions are obtained by mixing the above-mentioned compositions immediately before use.

10 These kits are well known in the art and the composition in each container can be manufactured utilizing any one of the standard approaches, these include:

- Oil in water process
- Phase Inversion process
- 15 • One-pot process

The chelants are usually added to a proportion of the water at the start of the making process at ambient temperature, and allowed to dissolve. The fatty components are then added and the mixture is processed as is normal for the above outlined procedures. For example, in a 1 pot process the polymers and 20 chelants would be predissolved in water, the fatty materials added and then the whole heated to about 70-80°C.

A controlled cooling and optional shearing process to form the final structured product in the case of an emulsion would then follow. Addition of the ammonia and pH trimming complete the making process of the dye cream.

25 In the case of a liquid solution comprising acrylate polymers, these would be formulated into the hydrogen peroxide component. The glycol solvents and fatty components are formulated into the dye component. A structured product is formed when the dye and hydrogen peroxide components are mixed together prior to use of the composition, through deprotonation of the polymer acrylic acid 30 groups yielding a polymeric micro-gel. Further details on the manufacture of these two-part aqueous composition for coloring hair, which forms a gel on

mixing of the two parts can be found in US 5,376,146, Casperson et al. and US 5,393,305, Cohen et al.

The composition of the present invention can also be formulated as 2-part aqueous compositions comprising polyetherpolyurethane as thickening agent
5 (such as Aculyn ® 46) as described in US6,156,076, Casperson et al. and US6,106,578, Jones.

When the compositions of different containers are mixed before use and the resulting mixture comprises the chelants claimed, there is no preference on how the chelants are distributed in these containers. Obviously chelants that can
10 be altered by hydrogen peroxide (or any oxidizing agent used) such as secondary amine chelants should however be formulated in the dye component. The hydrogen peroxide component should however preferably comprise at least about 0.1% of a stable chelant to stabilize hydrogen peroxide. This stabilizer is required to prevent the hydrogen peroxide from decomposing too rapidly. For
15 example EDTA can be used in the hydrogen peroxide component as stabilizer.

METHODS OF USE

It is understood that the examples of methods of use and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without
20 departing from the scope of the present invention.

Without pretreatment

The chelants according to the present invention are preferably formulated directly in the oxidizing compositions applied on hair (e.g. oxidative dye compositions or bleaches).

25 **Oxidative dye**

Oxidative dye compositions are usually sold as a kit comprising at least two separate containers: one contains the oxidative dye precursors with the hair-swelling agent (e.g. ammonia) in a suitable carrier (e.g. dye cream or liquid) and the other contains the oxidizing agent in a suitable carrier (e.g. hydrogen

peroxide cream or liquid). The consumer prepares the oxidative dye composition immediately before use by mixing both compositions and applies it on hair. After working the mixture a few minutes (to insure uniform application to all of the hair), the oxidative dye composition is allowed to remain on the hair for an 5 amount sufficient for the dyeing to take place (usually about 30 minutes). The consumer then rinses his/her hair thoroughly with tap water and allows it to dry. It is observed that the hair has changed from its original color to the desired color.

When present, the optional conditioning agent can be packaged partly or in totality in a third container. In this case, all three compositions can be mixed 10 immediately before use and applied together, or the content of the third container can be applied (after an optional rinse step) as a post-treatment immediately after the oxidative dye composition resulting from the mixture of the other containers.

Bleaching compositions

15 Bleaching compositions are usually sold as a kit comprising two or three separate containers. The first contains the hair-swelling agent (e.g. ammonia), the second contains the oxidizing agent and the third (optional) contains a second oxidizing agent (e.g. alkali or ammonium salt of persulphates, percarbonate, perborate). The consumer prepares the bleaching compositions 20 immediately before use by mixing all compositions and applies the mixture on hair (as for the oxidative dye composition) for an amount of time sufficient for the bleaching to take place (usually about 30mn).

In this kind of kit comprising at least two containers there is no preference 25 on the distribution of the chelants and conditioners in the containers, although it is preferred that the composition comprising the oxidizing agent comprises at least a small amount of chelant (which is not necessary a phosphonate chelant) to stabilize the oxidizing agent.

As for oxidative dye compositions, the optional conditioning agent can be packaged partly or in totality in a third container. In this case, all three 30 compositions can be mixed immediately before use and applied together, or the

content of the third container can be applied (after an optional rinse step) as a post-treatment immediately after the oxidative dye composition resulting from the mixture of the other containers.

With pretreatment

5 The chelants can also be applied to hair as a pre-treatment. The pretreatment composition ("first composition") can be applied immediately before the oxidizing composition ("second composition") or after a longer period of time.

Pretreatment immediately followed by an oxidizing composition

In the case of a pretreatment applied on hair and immediately followed by
10 the oxidizing composition, said pretreatment composition can be rinsed off hair
before the application of the oxidizing composition, but will be preferably kept on
the hair during the application of the oxidizing compositions, the resulting mixture
being rinsed off following the oxidizing step. Kits comprising one container for the
15 first composition (pre-treat) and one, two or more containers for the second
composition (oxidizing composition) can be advantageously used for this
method. Two containers or more can be required for the second composition in
case this second composition is prepared immediately before use by mixing the
content of two containers or more (e.g. oxidative hair dye composition or
bleaching composition). The kit can also comprise an additional container for a
20 composition comprising a conditioning agent that is applied independently from
the second composition in a third step, optionally following a rinsing step.

Color care

The pretreatment can also take place as a "color care" treatment anytime
between two oxidative treatments but not immediately prior to one. The 2
25 oxidative treatments are preferably separated by at least one day, more
preferably at least one week. Oxidative hair dye treatments are generally
repeated about once a month and obviously, hair will be usually rinsed with water
immediately after each oxidative treatment. The "color care" treatment can be

repeated as many times as practical between the two oxidative treatments, which can be once, twice or more.

WHAT IS CLAIMED IS:

1. A composition suitable for treating hair comprising:
 - a) an oxidizing agent;
 - b) a chelant;

5 wherein said chelant is in an amount sufficient to provide a damage benefit equivalent to less than 160, preferably less than 140, more preferably less than 120, even more preferably less than 110 cysteic acid units as measured by the FT-IR Damage Assessing Protocol after a 5-Cycle Oxidative Hair Treatment Protocol With 2 Intermediate Washes as defined herein and/or to provide a damage benefit equivalent to a Normalized Shine Ratio of at least 0.80, preferably at least 0.85, more preferably at least 0.95, even more preferably at least 0.99 as measured by the Goniophotometer Damage Assessing Protocol after a 5-Cycle Hair Oxidative Treatment Protocol With 10 Intermediate Washes as described herein.

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- 2. A composition according to Claim 1, wherein said composition comprises a chelant (L) having a $\frac{\log K_{CuL}}{\log K_{CaL}}$ ratio calculated at pH 10 of at least 3.20, preferably at least 3.30, more preferably at least 3.40, even more preferably at least 3.50; wherein $\log K_{CuL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Cu^{2+} and $\log K_{CaL}$ is the common logarithm of the Conditional Stability Constant of said chelant with Ca^{2+} .

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- 3. A composition according to Claim 2, wherein said chelant (L) has a Hydrogen Peroxide Decomposition Ratio (% Loss) of less than 10%, preferably less than 3.5%, even more preferably less than 2% as measured by the Hydrogen Peroxide Decomposition Ratio Measurement

Protocol described herein and/or said chelant forms a hexadendate complex with Cu²⁺.

4. A composition according to Claim 3, wherein said chelant (L) is an aminocarboxylic acid chelant selected from the group consisting of diamine-N,N'-dipolyacids, monoamine monoamide-N,N'-dipolyacids and N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid (HBED), salts thereof, derivatives thereof and mixtures thereof.
- 10 5. A composition according to Claim 4, wherein said polyacids contain at least two acid groups independently selected from the carboxylic acid group (-COOH), sulphonic group (-SO₃H), the o-hydroxyphenyl group, the m-hydroxyphenyl group and the p-hydroxyphenyl group.
- 15 6. A composition according to Claim 5 wherein said chelant is selected from the group consisting of ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediamine-N,N'-digtutaric acid (EDDG), 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPLDS), glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-bis(ortho-hydroxyphenyl acetic acid) (EDDHA), salts thereof, derivatives thereof and mixtures thereof.
- 20 7. A composition according to Claim 6 wherein said chelant is selected from ethylenediamine-N,N'-disuccinic acid, salts thereof, derivatives thereof and mixtures thereof.
- 25 8. A composition according to any of the preceding Claims, wherein the pH of the composition is above 8, preferably between 8 and 12, more preferably between 9 and 11.5, even more preferably between 9.5 and 11.

9. A composition according to any of the preceding Claims, wherein said composition is in the form of an oil-in-water emulsion or a thickened aqueous solution.
- 5 10. A composition according to any of the preceding Claims, wherein said oxidizing agent is present at a level of from 0.1% to 40% by weight of said composition and is selected from water-soluble oxidizing agents and mixtures thereof, preferably hydrogen peroxide.
- 10 11. A composition according to any of the preceding Claims, wherein said chelant is present at a level of from 0.01 to 10%, preferably from 0.5 to 5%, more preferably from 2% to 4% by weight of the composition.
- 15 12. A composition according to any of the preceding Claims, further comprising at least one oxidative hair dye precursor.
13. A method of treating hair comprising the step of contacting hair with a composition according to any of the preceding Claims.
- 20 14. A method of treating hair comprising the subsequent steps of:
 - i) applying a first composition comprising an oxidizing agent;
 - ii) applying a second composition comprising a chelant wherein said chelant is in an amount sufficient to provide a damage benefit equivalent to less than 160, preferably less than 140, more preferably less than 120, even more preferably less than 110 cysteic acid units as measured by the FT-IR Damage Assessing Protocol after a 5-Cycle Oxidative Hair Treatment Protocol With 2 Intermediate Washes as defined herein and/or to provide a damage benefit equivalent to a Normalized Shine Ratio of at least 0.80, preferably at least 0.85, more preferably at least 0.95, even more preferably at least 0.99 as measured by the Goniophotometer

Damage Assessing Protocol after a 5-Cycle Hair Oxidative Treatment Protocol With 10 Intermediate Washes as described herein; and

iii) applying a third composition comprising an oxidizing agent; wherein steps i) and iii) are separated by at least 1 day and step ii) does not take place immediately before step iii).

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15. A kit for dyeing hair comprising a first and a second compositions packaged in different containers, wherein said first composition comprises an oxidizing agent and said second composition comprises an oxidative dye precursor, characterized in that the resulting mixture of said first and 10 second compositions is a composition according to Claim 12.

15. A method of dyeing human hair comprising the subsequent steps of:
i) mixing the first and second composition of a kit according to Claim 15;
ii) applying the mixture obtained after step i) to hair;
iii) massaging said mixture into hair;
iv) retaining said mixture on the hair for an amount of time sufficient for mixture to dye the hair;
iv) rinsing off said composition with water.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/08481

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61K7/135

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61K C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 24106 A (DIAS LOUIS CARLOS ; PULLAN ROWENA JULIET FLUX (GB); SANGER ALISON J) 10 July 1997 (1997-07-10) cited in the application page 36, paragraph 2 -page 37, paragraph 4 page 18, last paragraph claims 1,19,20; examples 1,6	4-13;15, 16
A	US 6 024 891 A (HUGHES IAIN ALLAN) 15 February 2000 (2000-02-15) column 10, line 31 - line 51; claim 1 column 1, paragraph 2	4-7,11
A	EP 1 001 011 A (PROCTER & GAMBLE) 17 May 2000 (2000-05-17) paragraphs '0133!, '0135!; claims 1,2,7-11	4-10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

19 July 2002

Date of mailing of the international search report

31/07/2002

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/08481

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US 02/08481**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 1-3 14 because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-3 14

Present claims 2-16 relate to a composition defined (*inter alia*) by reference to the following parameters:

P1: logKCuL/logKCaL

P2: Hydrogen Peroxide Decomposition ratio

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the parts relating to the composition as described in cls. 4-13,15,16.

Present claims 1-16 relate to a composition defined by reference to a desirable characteristic or property, namely a damage benefit equivalent to less than 160 cysteic units and/or equivalent to a Normalized Shine Ratio >0.8.

The claims cover all compositions having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such compositions. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the compositions by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to the composition as described in cls. 4-13, 15,16.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.